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DoD EPA DOE **SERDP**

Strategic Environmental Research and Development Program

Improving Mission Readiness Through Environmental Research

FISCAL YEAR 1996 ANNUAL REPORT AND FIVE-YEAR (1996-2000) STRATEGIC INVESTMENT PLAN

March 1996

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This report provides the details of funds appropriated in Fiscal Years 1995 and 1996. The individual research projects were reviewed and selected by the Strategic Environmental Research and Development Program Council in response to specific defense mission-relevant environmental requirements for research and development. The *Strategic Environmental Research And Development Program Five-Year (1996-2000) Strategic Investment Plan* is based on an FY 1996 appropriation of $58.155 million. It is submitted on behalf of the Strategic Environmental Research and Development Program Council.

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FOREWORD

The Strategic Environmental Research and Development Program was established by 10 U.S.C. §§2901-2904. The Strategic Environmental Research and Development Program addresses environmental matters of concern to the Department of Defense and the Department of Energy. It is a Department of Defense Program planned, managed, and executed in full partnership with the Department of Energy and Environmental Protection Agency with participation by numerous other Federal and non-Federal organizations.

This report includes information required by 10 U.S.C. §2902 for the annual report to Congress. It provides the details of funds appropriated in Fiscal Years 1995 and 1996. The individual research projects were reviewed and selected by the Strategic Environmental Research and Development Program Council in response to specific defense mission-relevant environmental requirements for research and development. Prior to funding, all new start projects and continuing projects requiring more than $900,000 in FY96 were reviewed and recommended by the Strategic Environmental Research and Development Program Scientific Advisory Board. Their comments on each project are in the *Strategic Environmental Research and Development Program Scientific Advisory Board FY 1995 Annual Report* which has been forwarded to Congress from the Chair of the Scientific Advisory Board via the Chair of the Strategic Environmental Research and Development Program Council.

The *Strategic Environmental Research And Development Program Five-Year (1996-2000) Strategic Investment Plan* is based on an FY 1996 appropriation of $58.155 million. It is submitted on behalf of the Strategic Environmental Research and Development Program Council consisting of: the Director of Defense Research and Engineering; the Deputy Under Secretary of Defense (Environmental Security); the Vice Chairman of the Joint Chiefs of Staff and representatives from each of the uniformed Services and Coast Guard; the Director of the Department of Energy Office of Energy Research; the Assistant Secretary of Energy for Environmental Management; the Assistant Secretary of Energy for Defense Programs; and the Administrator of the Environmental Protection Agency.

ACRONYMS

Each acronym used in the text is defined in its first use. This section provides a summary list of acronyms.

A	U.S. Army
AAP	Army Ammunition Plant
AEC	Army Environmental Research Center
AEERL	Air and Energy Engineering Research Laboratory
AERL	Athens Environmental Laboratory
AF	U.S. Air Force
AFCEE	Air Force Center for Environmental Excellence
AFCESA	Air Force Civil Engineering Support Activity
AFM	Atomic Force Microscopy
AFOSR	Air Force Office of Scientific Research
AICUZ	Air-Installation Compatible Use Zone
Al	Aluminum
AL	Armstrong Laboratory
ALC	Air Logistics Centers
ANL	Argonne National Laboratory
ANSI	American National Standards Institute
AOP	Advanced Oxidation Process
AQMD	Air Quality Management Districts
ARA	Applied Research Associates
ARDEC	Army Armaments Research, Engineering & Development Center
AREP	Alternative Refrigerant Evaluation Program
ARM	Atmospheric Radiation Measurement
ARPA	Advanced Research Projects Agency
ARSAP	Atmospheric Remote Sensing and Assessment Program
ASTE	Advanced Strategic and Tactical Expendables
ATEDS	Advanced Technology Expendables and Dispenser System
ATLAS	Advanced Testing Line for Actinide Separations
ATMOS	Atmospheric Observing Satellite
ATRP	Automatic Target Recognition Processor
BAA	Broad Agency Announcement
BDC	Background Data Center
BLM	Bureau of Land Management

BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CAA	Chromic Acid Anodizing
CAAA	Clean Air Act Amendments
CAME	Clean Agile Manufacturing of Energetics
CARB	California Air Resources Board
CART	Cloud and Radiation Testbed
CATS	Controlled Archeological Test Site
CCAC	Close Combat Armament Center
CCD	Charge Coupled Devices
Cd	Cadmium
CER	Center for Environmental Research
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (called Superfund)
CERL	U.S. Army Construction Engineering Research Laboratory
CFC	Chlorofluorocarbons
CIA	Central Intelligence Agency
CP	Compliance Thrust Area
CPAT	Corrosion Prevention Advisory Teams
CPT	Cone Penetrometer
Cr	Chromium/Chromates
CRADA	Cooperative Research and Development Agreement
CRREL	U.S. Army Cold Region Research and Engineering Laboratory
CS	Conservation Thrust Area
CSS	Coastal Systems Station
CU	Clean Up Thrust Area
Cu	Copper
CUSP	Commander, Undersea Surveillance Pacific
D/NETDP	DoD/National Environmental Technology Demonstration Program
DCA	Dynamic Contact Angle Analyzer
DECIM	Defense Environmental Corporate Information Management Program
DFSS	Dedicated Feedstock Supply Systems
DMMF	Developmental Manufacturing and Modification Facility
DNA	Defense Nuclear Agency
DNAPL	Dense Non-Aqueous Phase Liquid
DNL	Dry Low NO_x
DoD	Department of Defense
DOE	Department of Energy
DOI	Department of the Interior

DPG	Dugway Proving Ground
DUECC	Defense Utility Energy Coordinating Council
DUSD(ES)	Office of the Under Secretary of Defense Environmental Security
EA	Environmental Assessment
ECIP	Energy Conservation Investment Program
ECP	Engineering Change Proposal
ECU	Environmental Control Unit
EDA	End-use Disaggregation Algorithm
EIS	Environmental Impact Statement
EMAA	Encapsulated Micron Aerosol Agents
EMAP	Environmental Monitoring and Assessment Program
EN	Energy Conservation/Renewable Resources Thrust Area
EO	Electro-Optic
EOS	Earth Observing System
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right to Know Act
ERDEC	US Army Edgewood Research, Development and Engineering Center
ESA	Endangered Species Act
EQ Strat Plan	Environmental Quality Technology Research and Development Strategic Plan
EQT	Environmental Quality Technology Program
EXCEL	Experimental Chloride Extraction Line
FAA	Federal Aviation Administration
FEDS	Federal Energy Decision Screening Model
FEMP	Federal Energy Management Program
FID	Free-Induction Decay
FORS	Fiber Optic Raman Sensor
FOX	Fluoroalkoxymethyl-3methyl-Oxetane
FS	Feasibility Study
FTS	Fourier Transform Spectrometer
FWPPCA	Federal Water Pollution Prevention and Control Act
GAC	Granular Activated Carbon
GC	Gas Chromatography
GCDIS	Global Change Distributed Information System
GC/MS	Gas Chromatography/Mass Spectrometry
GCM	Global Climate Monitoring
GCW	Groundwater Circulation Well
GEC	Global Environmental Change Thrust Area

GIMI	Global Imagery Monitor of the Ionosphere
GHP	Geothermal Heat Pumps
GIS	Geographic Information System
GISS	Goddard Institute for Space Studies
GOCO	Government-Owned/Contractor-Operated
GOES	Geostationary Operational Environmental Satellites
GPS	Global Positioning System
GRASS-PRISM	Geographic Resource Analysis Support System - Planning and Resource Integration Stewardship Model
GSE	Ground Support Equipment
GV	Grassland Value Function
H_2O_2	Hydrogen Peroxide
HAZMAT	Hazardous Materials
HAZMIN	Hazardous Waste Minimization
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HMX	Octahydro-1,3,5,7-Tetranitro 1,3,5,7-Tetrazocine
HOPS	Heuristic Optimized Processing Systems
HPLC	High Performance Liquid Chromatography
HUD	Department of Housing and Urban Development
HW	Hazardous Wastes
HWRC	Hazardous Waste Research Center
IBEAM	Installation Baseline Energy Analysis Model
ICUZ	Installation Compatible Use Zone
IDLAMS	Integrated Dynamic Landscape Analysis and Modeling System
IHDIVNAVSURF-WARCEN	Indian Head Division, Naval Surface Warfare Center
INEL	Idaho National Engineering Laboratory
IPD	Integrated Product Development
IPPD	Integrated Product/Process Development
IRP	Installation Restoration Program
ISB	In Situ Bioremediation
IUSS	Integrated Undersea Surveillance System
IVD	Ion Vapor Deposited
JATO	Jet Assisted Take Off
JETC	Jet Engine Test Cell
JHU/APL	John Hopkins University Applied Physics Laboratory
JPL	Jet Propulsion Laboratory

LAAP	Louisiana Army Ammunition Plant
LAMS	Laser Ablation Mass Spectroscopy
LANL	Los Alamos National Laboratory
LARPS	Large Aircraft Robotic Paint Stripping
LCA	Life Cycle Assessment
LCAAP	Lake City Army Ammunition Plant
LIBS	Laser-Induced Breakdown Spectroscopy
LIF	Improved Laser-Induced Fluorescence
LIN	Liquid Nitrogen
LIS	Laser Ignition System
LLNL	Lawrence Livermore National Laboratory
LMS	Lead Hazard Mitigation Management System
LNAPL	Light Non-Aqueous Phase Liquid
LOVA	Low Vulnerability Ammunition
LRS&T	Long Range Science and Technology Program
MADOM	Magnetic and Acoustic Detection of Mines
MAHRSI	Middle Atmospheric High Resolution Spectrograph
MARPOL	International Maritime Organizations Marine Pollution Convention
MAS	Millimeter-Wave Atmospheric Sounder
MB/MS	Molecular Beam/Mass Spectrometric
MCFC	Molten Carbonate
MECL	Methylene Chloride
MEK	Methyl Ethyl Ketone
MM	Modifier Molecules
MMATS	Marine Mammal Acoustic Tracking System
MMPA	Marine Mammals Protection Act
Mn	Manganese
MODIS	Moderate-Resolution Imaging Spectroradiometer
MPC	Mobile Power Center
MR/H	Mine Reconnaissance/Hunter
MRTFB	Major Range and Test Facility Base
MTR	Military Training Routes
MTV	Magnesium-Teflon-Viton
MUDSS	Mobile Underwater Debris Survey System
MWCO	Molecular Weight Cutoff
MWOs	Modification Work Orders
N	U.S. Navy
NADEP	Naval Depots

NAPL	Non-Aqueous Phase Liquid
NASA	National Aeronautics and Space Administration
NAVFAC	U.S. Navy Engineering Facilities Command
NBS	National Biological Survey
NCAR	National Center for Atmospheric Research
NDFT	Non-local Density Functional Theory
NDSC	Network for Detection of Stratospheric Change
NEPA	National Environmental Policy Act
NESHAP	National Emission Standard for Hazardous Air Pollution
NFESC	Naval Facilities Engineering Service Center
NGB	National Guard Bureau
NHPA	National Historic Preservation Act
Ni	Nickel
NMERI	New Mexico Engineering Research Institute
NMR	Nuclear Magnetic Resonance
NOAA	National Oceanic and Atmospheric Administration
NOV	Notice of Violation
Nox	Nitrogen Oxide
NPS	National Park Service
NRaD	Naval Research and Development Center
NRL	Naval Research Laboratory
NSPS	New Source Performance Standards
NTIS	National Technical Information Service
O_3	Ozone
O&M	Operations and Maintenance
OB/OD	Open Burning/Open Detonation
OC-ALC	Oklahoma City Air Logistics Center
ODC	Ozone Depleting Chemicals
ODS	Ozone Depleting Substances
OEM	Original Equipment Manufacturer
OH	Hydroxyl Radical
OOAM	Orbiting Ozone and Aerosol Monitor
OPC	Organophilic Clays
OTD	Office of Technology Development
PAFC	Phosphoric Acid Fuel Cells
PAH	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCA	Tetrachloroethane

PCB	Polychlorinated Biphenyls
PEO/FAS	Program Executive Officer for Field Artillery Systems
PEP	Propellants, Explosives, Pyrotechnics
PI	Principal Investigator
PNL	Pacific Northwest Laboratory
POAM	Polar Ozone and Aerosol Monitor
POL	Petroleum, Oil, Lubricants
POPS	Peroxone Oxidation Pilot System
PP	Pollution Prevention Thrust Area
ppb	Parts Per Billion
PTT	Platform Transmitting Terminals
PVD	Physical Vapor Deposition
PVRC	Photovoltaic Review Committee
QA/QC	Quality Assurance/Quality Control
QMP	Quality Management Plan
R&D	Research and Development
RAIDS	Remote Atmospheric and Ionospheric Detection System
RCRA	Resource Conservation and Recovery Act
RDT&E	Research, Development Test & Evaluation
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
REEP	Renewable and Energy Efficiency Planning
REMPI	Resonance-Enhanced Multiple Photon Ionization
RMA	Rocky Mountain Arsenal
ROI	Return on Investment
RREL-EPA	Risk Reduction Engineering Laboratory - Environmental Protection Agency
RSKERL	Robert S. Kerr Environmental Research Laboratory
RTG	Room Temperature Gradiometer
S-O&CS	Smokes, Obscurants & CS agents
SAB	Scientific Advisory Board
SAPT	Symmetry Adapted Perturbation Theory
SAR	Structural Activity Relationships
SBAA	Sulfuric-Boric Acid Anodize
SBIR	Small Business Innovation Research
SCAMP	Subsurface Cleanup and Mobilization Processes
SCAPS	Site Characterization and Analysis Penetrometer System
SCWO	Supercritical Water Oxidation
SDI	Strategic Defense Initiative
SEM	Scanning Electron Microscope

SERDP	Strategic Environmental Research and Development Program
SF	Supercritical Fluid
SIFDT	Selected Ion Flow-Drift Tube
SMCA	Single Manager for Conventional Ammunition
SNL	Sandia National Laboratory
SNRM	Strategic Natural Resources Management
SRTC	Savannah River Technology Center
STR	Synthetic Tandem Repeat
SW	Shallow Water
TAMU	Texas A&M University
TAP	Technical Advisory Panel
TCE	Trichloroethylene
TDL	Tunable Diode Laser
TES	Threatened and Endangered Species
TIPPP	Tidewater Interagency Pollution Prevention Program
TIWET	The Institute for Wildlife and Environmental Toxicology
TNT	Trinitrotoluene
TPE	Thermal Plastic Elastomer
TTAWG	Technology Thrust Area Working Group
TSVP	Thermal Spray Vitrification Process
UARS	Unmanned Air Reconnaissance System
UAV	Unmanned Aerospace Vehicle
UFA	Unsaturated Flow Apparatus
UM	University of Minnesota
USACERL	U.S. Army Corps of Engineers, Construction Engineering Research Laboratories
USACE	United States Army Corps of Engineers
USDA	United States Department of Agriculture
USFWS	US Fish and Wildlife Service
USGCRP	U.S. Global Change Research Program
USGS	U.S. Geological Survey
UST	Underground Storage Tank
UV	Ultraviolet
UVRS	Ultraviolet Remote Sensing
UXO	Unexploded Ordnance
VAAP	Volunteer Army Ammunition Plant
VLA	Vertical Line Arrays
VOC	Volatile Organic Compound

VPI	Virginia Polytechnic Institute and State University
VSW	Very Shallow Water
WES	U.S. Army Engineer Waterways Experiment Station
WIC	Water-Injected Combustor
WHV	Wildlife Habitat Value Function
WS	Weapon Systems
XCRIS	X-windows-based Cultural Resource Information System
XPS	X-ray Photo-Electron Spectroscopy
XRD	X-ray Diffraction
XRS	X-ray Spectrometry
Zn	Zinc

ANNUAL REPORT

Introduction

The Department of Defense (DoD) and Department of Energy (DOE) have, in many ways, mirrored society as a whole in their handling of defense-related environmental issues. The unique processes, procedures, and materials developed and/or used for defense applications, were sometimes implemented with little understanding of their environmental impact. More recently, new information and understanding of the negative impacts have initiated aggressive measures to rectify problems created as a result of past actions, to address current regulatory compliance issues, and to anticipate future environmental issues.

As our defense posture adjusted to new requirements in the early 1990's, the Strategic Environmental Research and Development Program (SERDP) was established by Congress in Public Law 101-510 (Title 10, U.S.C., §§2901-2904) as a DoD program planned and executed in partnership with DOE and the Environmental Protection Agency (EPA) to:

(1) Address environmental matters of concern to the DoD and the DOE through support for basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations.

(2) Identify research, technologies, and other information developed by the DoD and the DOE for national defense purposes that would be useful to governmental and private organizations involved in the development of energy technologies and of technologies to address environmental restoration, waste minimization, hazardous waste substitution, and other environmental concerns, and to share such research, technologies, and other information with such governmental and private organizations.

(3) Furnish other governmental organizations and private organizations with data, enhanced data collection capabilities, and enhanced analytical capabilities for use by such organizations in the conduct of environmental research, including research concerning global environmental change.

(4) Identify technologies developed by the private sector that are useful for DoD and DOE defense activities concerning environmental restoration, hazardous and solid waste minimization, and prevention, hazardous material substitution, and provide for the use of such technologies in the conduct of such activities.

The SERDP is the DoD's Corporate environmental science and technology (S&T) program and technology transfer mechanism. It fully leverages the complementary programs found within the uniformed Services, and those of DOE and EPA. The SERDP Council has implemented policies that take full advantage of the inherent capabilities of the participating organizations and has directed the development and execution of the Program consistent with the SERDP authorizing language.

SERDP identifies and develops technology to enhance capabilities to meet the environmental commitments of the DoD and those environmental requirements of the DOE that are of common interest to the DoD. It also serves to foster the exchange of scientific information and technologies among the participants, other governmental agencies, and the private sector. The SERDP leverages and interacts with other environmental programs to: identify and solve defense specific needs, extend applications of defense

information to others, and build on existing science and technology to derive more useable and cost-effective approaches for achieving reductions in environmental risks.

The SERDP FY 1995 appropriation was substantially reduced from FY 1994 levels ($160 million to $61.9 million). In response to this reduction, the SERDP Council acted to more sharply focus SERDP funding on the four major environmental areas of concern within the DoD: Cleanup, Compliance, Conservation and Pollution Prevention. All SERDP projects must address high priority defense mission-relevant environmental requirements as defined by the Deputy Under Secretary of Defense for Environmental Security. Although significant, unique research efforts in the Global Environmental Change and Energy Conservation/Renewable Resources Thrust Areas have produced substantive results, most only indirectly influence defense environmental requirements. Thus, a transition to this revised focus began in FY 1995 and will be completed by the end of FY 1996. However, SERDP will continue to investigate and employ global environmental change and energy conservation technologies to better address other environmental problems even after individual efforts are completed in FY 1996.

Program Management and Oversight

Council Actions

After experiencing significant reductions in the FY 1995 SERDP appropriation, the Council met in February, 1995 to approve a revised SERDP Strategic Guidance. SERDP was not in the position to satisfy every priority or each existing project. Consequently, the Council approved two specific recommendations to the Strategic Guidance:

1) Select Global Environmental Change and Energy Conservation/Renewable Resources projects would be completed by the end of FY 1996; and

2) Execution of the FY 1995 Program and planning for the FY 1996 Program would be accomplished in an 18 month period in order to place the Program on budget cycle at the beginning of FY 1996.

The Council voted unanimously to require that all SERDP projects must address high priority, defense mission-relevant environmental requirements (those in Cleanup, Compliance, Conservation and Pollution Prevention) as defined by the Deputy Under Secretary of Defense for Environmental Security. Although significant, unique research efforts in the Global Environmental Change and Energy Conservation/Renewable Resources Thrust Areas have produced substantive results, most only indirectly influence defense environmental requirements. Thus, a transition to this revised focus began in FY 1995 and will be completed by the end of FY 1996. However, SERDP will continue to investigate and employ global environmental change and energy conservation technologies to better address other environmental problems even after individual efforts are completed in FY 1996.

Reductions to the FY 1995 appropriation were made, for the most part, as a result of the SERDP being out of phase with the budget cycle and, accordingly, not consistent with DoD's obligation and expenditure goals. The top priority of the Council, therefore, was to place the Program on budget cycle and ensure that the scarce resources allocated to SERDP were used effectively and efficiently.

In consort with the Executive Working Group, the Executive Director received this Strategic Guidance and prepared a responsive FY 1995 Program. This Program was quickly approved by the Council in

April, 1995. Concurrently, the Executive Director and the Executive Working Group were preparing the FY 1996 Program. Through collective persistence and effective management of the SERDP participants, as well as superb individual efforts of the Technology Thrust Area Working Groups, the FY 1996 Program was in place and approved by the Council in August, 1995. *For the first time in SERDP's history, the Program was prepared to release appropriated funds at the beginning of the year in which they were appropriated.*

In remarks to the Council at their meeting in August of 1995, Dr. Marvin Moss, Provost and Vice Chancellor for Academic Affairs at the University of North Carolina at Wilmington and Chair of the SERDP Scientific Advisory Board, shared his thoughts on SERDP's progress during the year. Dr. Moss strongly endorsed the FY 1996 Program and stressed the importance of preparing the Program prior to the beginning of FY 1996. He emphasized that quality is often the metric for an R&D program and provided examples of SERDP projects as representative of high quality projects. In sum, Dr. Moss reiterated his endorsement for SERDP, and he was confident that SERDP is meeting the intent, goals and objectives of Congress.

As their final action of the year, the Council approved the Strategic Guidance for the FY 1997 SERDP program build. The Council directed the Executive Director to view the program build from the perspective of how the SERDP integrates itself with the national effort: preclude duplication of research efforts, leverage other environmental programs, and continue to strive for congruency with the Administration's goals.

Focus

In compliance with this guidance, SERDP planned the FY 1996 Program by continuing to focus on four key elements in order to facilitate success:

(1) address the highest priority, defense relevant environmental requirements with a sharper focus on multi-Service issues;

(2) ensure that world-class researchers are planning and performing the research;

(3) aggressively transfer SERDP results to the users and/or the next steps of development, demonstration, or commercialization; and

(4) comply with current DoD fiscal guidance.

The SERDP Executive Director aggressively addressed each item.

The Executive Director and his Program Managers worked hand-in-hand with the office of the Deputy Under Secretary of Defense for Environmental Security to establish clear lines of communication, effectively address the Department's highest priority environmental requirements, and foster transition of technical efforts to field demonstration or implementation. Through the use of tailored statements of need, the Executive Director solicited cooperatively funded and performed projects to address high priority multi-Service needs. The Technology Thrust Area Working Groups (TTAWG), SERDP's multi-Agency planning and coordinating bodies, facilitated this process through effective communications and understanding the needs and capabilities of the federal R&D infrastructure. By focusing on multi-Service needs, the projects acquired a level of funding and performing expertise that would not normally be attained in a single Service effort.

Another evaluation criteria for project selection is the credentials of the Principal Investigator and associate performers on the project. World-class research is considered the cornerstone of SERDP projects, and the SAB, TTAWGs and the Executive Director all ensure that the research team demonstrates the highest standards of research and superior technical merit.

SERDP is completing its fourth year of technology development. Accordingly, many of the projects began in the earlier years are being completed and are now ready for implementation or transition to the next step of development. SERDP has taken steps to aggressively facilitate this transfer.

Strict compliance with DoD fiscal policy ensures that SERDP projects can move rapidly to a successful conclusion and contribute to environmental solutions. Through the continuous monitoring of project technical and fiscal performance, the Executive Director is able to take aggressive, corrective action to promote effective use of scarce R&D resources.

Involvement of Academia and Industry

In FY 1995, slightly over 65% of all funds were used by industry, not-for-profit organizations, or universities via contracts, interagency agreements, cooperative R&D agreements and grants. This figure has remained relatively constant over the life of the SERDP, and it is anticipated to remain so in the future.

Technology Transfer and Information Exchange

Transferring technology into field use is a principle goal of SERDP. Accordingly, SERDP management has taken significant steps to facilitate and enhance technology transfer and transition.

SERDP organized and held its first annual Symposium in April 1995 - a technical exposition that attracted nearly 500 attendees in the Washington, D.C. area to hear keynote policy addresses, 63 technical presentations and to view 94 exhibits - all of which provided an outstanding forum to exchange the latest defense-relevant, environmental technology information and ideas. The second Symposium is scheduled for November 1996. It will continue to promote environmental science and technology that benefit the DoD mission accomplishment. All SERDP efforts have direct or indirect application to the commercial sector.

The SERDP Quarterly Information Bulletin increased distribution to over 3,200 people at all levels of the private and governmental sectors. The Bulletin featured SERDP accomplishments, articles on management initiatives, and highlights of Program development issues. A complete listing of SERDP products' is included annually in the Bulletin to ensure that the entire readership is aware of all available SERDP results including reports, papers, videos, and other publications.

A SERDP Home Page was placed on the Internet World Wide Web to provide even broader distribution of Program information. The Home Page (http:www.wes.army.mil/serdp/home.html) allows users of the Internet to become familiar with SERDP goals and objectives, technical areas of interest, planning calendars, performers, management structure, and program results. Plans for the future include providing technology area summary data and SERDP performers with associated hypertext information links to describe the work being performed at various locations.

Several SERDP projects have technology information transfer as their primary goal. In Pollution Prevention, the EPA leads a project entitled, "Integrated Solvent Substitution Data Base", having a

common name of "EnviroSense". EnviroSense links and shares information from the data bases of several Federal Agencies and Associations that focus on substitutes for hazardous solvents. Users of this data base can easily conduct a search for acceptable substitutes that are requirement specific. Another project, the "DoD/National Environmental Technology Demonstration Program", cooperates with the regulators, stakeholders, and industry to conduct standardized, controlled remediation technology demonstrations. Results are standardized and well-documented. Validation of these technologies may also be conducted on these sites with contributing funds from other R&D programs, such as the Environmental Security Technology Certification Program.

Significant Technical Accomplishments by Thrust Area

The following paragraphs are examples of significant accomplishments from representative SERDP projects.

Major Cleanup Accomplishments:

Pilot Scale Peroxone Treatment of Contaminated Groundwater - The US Army Waterways Experiment Station, completed pilot testing of the Peroxone Oxidation Pilot System (POPS) in August 1994. This portable prototype system is used for ex situ remediation of organic groundwater contaminants, including explosives. Test results indicated nearly complete breakdown (below detection levels) of the contaminants of concern. When fully developed, the Peroxone process offers the potential for an order of magnitude cost savings over currently accepted best technology ($0.50/kgal versus $4.00-$5.50/kgal). Considering the hundreds of millions of gallons of contaminated groundwater, this technology has significant potential benefit to the DoD, other Federal agencies, and private industry.

This research uses leveraged funding from DoD's Strategic Environmental Research and Development Program, the US Army's Environmental Quality Technology RDT&E program, and the Program Manager at Rocky Mountain Arsenal.

Site Characterization and Analysis Penetrometer System (SCAPS) Saves Time and Money - Traditional methods of characterizing contaminant sites incorporate drilling, sampling, and off-site laboratory analysis, and are costly and time-consuming. It is estimated that costs for site investigations could be reduced by at least 50% for every contaminant for which a reliable in situ chemical sensor were available.

The Site Characterization and Analysis Penetrometer System (SCAPS) has shown the capability to rapidly screen contaminated sites. SERDP is supporting the accelerated development of additional sensors to be mounted on SCAPS, including sensors to detect explosive compounds, petroleum products, solvents, and heavy metals. SCAPS technology is expected to reduce the costs of traditional site screening by up to 90%, increase the number of data points by up to 400%, and significantly reduce the required time. Currently there are estimated to be over 300 DoD sites with leaking underground storage tanks which could be characterized using this technology, and that is only one of many potential applications.

New Tracer Will Enhance DoD Cleanup - Low-solubility organics such as chlorinated solvents were used and released to the environment in massive quantities during the 50's, 60's, and 70's. These contaminants have migrated through the subsurface and entered ground water at over 2000 DoD sites. The greatest barrier to satisfactorily remediating these sites is a lack of cost-effective technologies for restoring the ground water quality, particularly when nonaqueous-phase liquids (NAPLs) are present. Estimates of

the cost to clean up these sites range up to hundreds of billions of dollars. One of the major difficulties in aquifer remediation is determining the extent and distribution of the NAPL in contaminated aquifer formations.

Under SERDP sponsorship, the EPA's National Risk Management Research Laboratory, the University of Florida, and the University of Texas at Austin have developed a tracer procedure that provides an improved ability to characterize sites with NAPL contamination. This procedure can provide a substantial improvement over traditional monitoring wells and core samples in certain subsurface environments and was successfully applied in a highly controlled field experiment in a contaminated cobbly, sandy gravel aquifer at Hill AFB, Utah. The tracer results provided reproducible descriptions of the NAPL contaminant distribution, while the size and quantity of the cobbles in the formation made it extremely difficult to collect and interpret core samples. The tracer test was developed to characterize the effectiveness of several subsurface extraction technologies that are undergoing a comparative evaluation at the Hill AFB site. Additional tracer tests will be run over the next year to perfect the procedure.

Phytoremediation in SERDP: An Emerging In-Situ Cleanup Technology With Exciting Potential - Phytoremediation is the use of engineered plant or algae ecosystems to clean up contaminated soils, groundwater, or industrial waste streams. SERDP funded one of the very first Phytoremediation research projects to cleanup organic contaminants in 1992 at the Ecosystem Research Division of the Environmental Protection Agency's National Exposure Research Laboratory in Athens, GA (NERL-Athens). NERL-Athens discovered four natural processes in sediments that were all traced to stable plant proteins. A field immunoassay uses antibodies to find the reductive nitroreductase and dehalogenase enzymes in plants, making it possible to ecologically engineer local plants into wetlands and other ecosystems for natural clean up. Mass balances prove that TNT, solvents and all metabolites are completely degraded, not accumulated. Pilot studies at Alabama AAP with Auburn University and Tyndall Air Force Base showed that Eurasian watermilfoil degraded soil TNT from 5000 ppm to levels of 30 ppm. SERDP funding of $1 million allowed Georgia Tech and Rice University to define how treatability studies should be conducted for groundwater and soil cleanup of TNT.

SERDP's Federal Integrated Biotreatment Consortium integrated the Phytoremediation advances by ERD-Athens into the overall technology development goals for SERDP. Early spinoffs include innovative plant selection for wetlands at Iowa Army Ammunition Plant and an Environmental Security Technology Certification Program demonstration to cleanup groundwater at Milan Army Ammunition Plant. Rapid progress continues under the Consortium to develop soil cleanup methods for explosives and groundwater cleanup methods for solvents. This Phytoremediation project is an excellent reflection of the SERDP vision to team and redirect science and engineering excellence in EPA, DoD, DOE, and university laboratories. Well directed SERDP support has reduced the demonstration time by five years and costs by $2 million compared to other innovative biotreatments for explosives.

SERDP Facilitates Technology Demonstration, Transfer, and Regulatory Acceptance with the DoD/National Environmental Technology Demonstration Program - During FY 1995, SERDP conducted or initiated 16 demonstrations at five demonstration sites around the U.S. to conduct prototype field demonstrations of relevant, innovative cleanup technologies. Upon successful completion, these technologies are candidates for the DUSD(ES) Environmental Security Technology Certification Program to validate its performance, or for direct use in the field. Over the next five years, this program is scheduled to conduct over 100 demonstrations for a variety of soil and ground water contaminants.

Major Compliance Accomplishments:

Molten Glass Spraying Inhibits Escape of Lead-Based Paint - Recent tests supported by the Strategic Environmental Research and Development Program at the U.S. Army's Construction Engineering Research Laboratories (USACERL) indicate that a glass composition containing 14% iron oxide can reduce the leaching rate of lead from 30 ppm to less than 5 ppm. This combination of technology has the potential for solving a significant hazardous waste problem during the demolition of buildings whose interiors or exteriors have been coated with lead-based paint. If successful, this technology will substantially reduce the costs associated with renovation through reduced hazardous waste disposal costs and fugitive dust emissions. The same designer glass composition can immobilize chromium and cadmium as well and make the paint waste non-hazardous. The Thermal Spray Vitrification Process (TSVP) patented by USACERL is being transitioned to the Environmental Security Technology Certification Program for demonstration/validation of paint removal in Navy ships and DoD coastal steel structures such as hangar doors. It is probable that DoD's estimated $1.0B costs associated with lead based paint removal and disposal would be reduced 30-40%, with widespread applications beyond DoD.

Encapsulation of Hazardous Ions in Smectite Clays - The cost of disposal of hazardous metal ions is increasing as disposal sites become filled. Clay minerals, and other intercalation compounds such as zeolite, have been proposed for storing hazardous ions. However, clay is naturally hydrophilic so the ions enclosed within the clay would be susceptible to leaching by water.

Under SERDP sponsorship, DOE's Argonne National Laboratory has developed a process for modifying the surface of natural clays to create a hydrophobic clay after the hazardous ions have been introduced into it. After using the process, natural clays float on water, despite having a density higher than that of the liquid. The flotation characteristics have been unchanged after fifteen months and analysis has shown that, under an inert atmosphere, the organic coatings are stable to 500 degrees Centigrade. If additional long-term leaching tests confirm these initial findings, using clays to dispose of hazardous metal ions could substantially reduce both the need for hazardous waste landfills and the cost of disposing of these types of hazardous wastes.

Better Characterization of Open Burning/Open (OB/OD) Detonation Emissions Equates to Future Cost Savings - For more than 40 years, open burning/open detonation (OB/OD) has been the disposal method of choice for unwanted energetic materials. Although these methods have proven to be the fastest and cheapest available, they are being increasingly challenged by federal and state environmental regulators and a variety of civic action groups. Dense clouds that are characteristic of OB/OD operations appear threatening and, in the absence of scientific information to the contrary, it is widely assumed that these emissions are dangerous. In an attempt to investigate methods with which to gather sound scientific information, the U.S. Army Armament, Munitions, and Chemical Command (AMCCOM) initiated a large-scale field experiment in 1985 to determine the feasibility of obtaining data on OB/OD-generated emissions. From this beginning, a testing system known as the Bangbox has evolved under the partial sponsorship of SERDP. This testing system characterizes OB/OD emissions to the satisfaction of the U.S. EPA and a growing number of state regulators. It can test a wide variety of munitions and propellants. Testing is underway to determine the actual emissions produced by OB/OD disposal methods, and U.S. EPA representatives are collaborating in the effort. Eventually, researchers hope to be able to group munitions by emissions families, thereby obviating the need for testing all munitions. Full acceptance of this data may allow the Department of Defense to save millions of dollars by resuming certain OB/OD operations to dispose of many obsolete munitions, propellants and production waste.

Shipboard Greywater Treatment System Begins Pierside Evaluation - A system for treating shipboard Greywater (waste water from hotel services such as laundries and galleys) has been developed by the Navy's Carderock Division, Naval Surface Warfare Center under joint support from the Strategic Environmental Research and Development Program and the Navy's Environmental Program. A 4000 - gallon per day prototype system, based on three years of laboratory evaluation, has been installed at the U.S. Naval Base in Norfolk, VA, to treat the Greywater from the USS L.Y. SPEAR (AS-36), a submarine tender. After treatment, the waste water will meet anticipated U.S. and International discharge standards for Greywater in local contiguous zones and MARPOL Special Areas. Prototype data will provide the final design parameters for a shipboard system.

Major Conservation Accomplishments:

Marine Mammal Acoustic Tracking System is Big Cost Saver to Navy Ship-Shock Tests - Under funding by DoD's Strategic Environmental Research and Development Program, the Naval Research and Development Activity, San Diego California, developed the Marine Mammal Acoustic Tracking System (MMATS). MMATS provides a field of up to ten sonobuoys deployed by aircraft, and a neural net detector and tracker mounted inside the aircraft. The system can detect, differentiate by species, and track blue, fin, humpback, and sperm whales by their calls.

During the spring of 1994, MMATS was used to resolve a court injunction against the Navy regarding ship shock tests of the USS JOHN PAUL JONES. The tests involved detonating a number of 10,000-lb explosive charges at increasingly close ranges to the vessel, while the performance of systems aboard the vessel was closely monitored.

Within weeks of the scheduled start of the tests, the Natural Resources Defense Council won a temporary injunction to halt the test on the grounds of whale endangerment. Costs associated with the delay were approximately $150,000 per week. The injunction was lifted only when the Navy demonstrated MMATS' ability to warn of whales approaching within two miles of the test site. As a requirement for lifting the injunction, the court stipulated that MMATS must be used during the tests. MMATS performed superbly, on three occasions delaying a detonation until a blue whale had cleared the area. The SERDP-supported MMATS technology thus played a crucial role in avoiding the cancellation of a $68M testing effort while at the same time ensuring whale safety. MMATS is now a fully operational technology.

The Effects of Aircraft Overflights on Birds of Prey - SERDP is supporting the proof-of-concept of a dose-response model for predicting the effects of aircraft overflights on birds of prey. Results will be used to prepare more accurate Environmental Impact Statements concerning the environmental effects of flight operations -- a concern that has stopped proposed flight plans in the past. Results will also be used to help determine methods to mitigate adverse effects, if any are found.

This "raptors model" was developed at the Armstrong Laboratory, and is being tested in conjunction with the University of Alaska, Fairbanks, the Alaska Cooperative Fish and Wildlife Research Unit (National Biological Service), and Alaska Biological Research, Inc. It will comprise one module of the Air Force's Assessment System for Aircraft Noise.

The Yukon Military Operating Areas in Alaska were chosen as the test locations since large populations of peregrine falcons and bald eagles are located there, and these species are not threatened as in the continental United States. A three-day test was performed in July 1994 to set design parameters for the study and get a preliminary idea as to potential reactions of adult birds during jet overflights. Preliminary

indications showed that while the birds adopted alert positions, they did not abandon their nests or show other signs of panic. Additional tests will be completed during the next two years to define short and long term effects of noise stress.

SERDP Provides New Paradigm for Managing Threatened and Endangered Species Habitats on Regional Scales - The growing numbers of threatened, endangered, and sensitive species (TES) on military lands have resulted in constraints to training and testing on many installations. To date, most efforts to address TES issues have been conducted on a species by species basis on separate installations, but this approach has proven inadequate to account for the multitude of complex interactions that are critical to developing successful management strategies. SERDP is supporting the development of a regionalized approach to TES management on DoD lands designed to provide effective guidelines for managing both plant and animal TES. The Southeastern U.S. (including over 80 military installations in portions of 12 states) will be the initial region of focus. These efforts will then be adapted to other regions and will contribute substantively to a comprehensive, systematic, and integrated approach necessary for effective, mission-enhancing, TES management on all U.S. military lands.

SERDP Develops New Techniques To Facilitate Military Training and Testing - DoD's ability to conduct mission essential training and testing exercises is often severely limited by its lack of understanding of and inability to cost-effectively manage critical natural resources in consort with training and testing. In order to implement a cost-effective strategy, DoD needs more meaningful and easier to use assessment and management tools. Under partial funding by DoD's SERDP, the multi-agency Biodiversity Research Consortium (BRC) is providing many of the tools and understanding necessary for DoD to provide critically necessary training and testing in an environmentally enhancing and sustaining way. The BRC has developed techniques for prioritizing resource allocation with respect to biodiversity and habitat. The BRC has also developed and demonstrated a method that successfully shows the potential impacts of future land use scenarios on the hydrology, land use, and wildlife of military installations and their surrounding regions. BRC has provided these new tools to Camp Pendleton to help them prioritize risks and make impact assessments with respect to their training and testing activities. The effort has the direct support from the Camp Pendleton Commanding General. In addition to direct military mission support, these tools allowed Camp Pendleton personnel to interact more effectively with the surrounding Planning Agencies/Authorities (e.g. San Diego Association of Governments) regarding the future development of the entire region.

Major Energy Conservation/Renewable Resources Accomplishments:

New Energy Model Applied DoD Wide - Current National energy policy requires all federal facilities to reduce energy consumption and costs by 30% from 1985 to 2005. Under SERDP sponsorship, the U.S. Army Construction Engineering Research Laboratories developed the Renewable and Energy Efficiency Planning (REEP) model which provides DoD-wide estimates of the energy saving potentials for program planning and budgeting purposes. Energy statistics from over 200 military installations are contained in the REEP model database. The DoD Energy Policy Office used the REEP model to determine the multi-year DoD budget for meeting the Energy Policy Act of 1992 and Fort Polk used the model for their "Shared Energy Savings Project" which included installing geothermal heat pumps at 4000 family housing units. The Air Force, Army and Navy are currently using it to update their energy programs. In addition to DoD, the University of Illinois, the city of Carson, California, and several architect/engineering firms are using the REEP model to plan and evaluate improvements to their energy conservation programs.

Reduced Atmospheric Emissions in DoD - DoD is the largest, single, centrally managed user of energy in the world with annual energy pollution emissions estimated at 12.2 million tons of carbon dioxide, 160 thousand tons of nitrogen oxide, and 169 thousand tons of sulfur oxide.

Photovoltaics (PV) technology can significantly reduce both life cycle cost and environmental degradation, especially in areas where DoD generates its own electrical power. PV's long term potential translates to 33 percent less emissions, and savings of $1.6 billion per year. With full SERDP sponsorship, Sandia National Laboratories successfully demonstrated the power processing technology for Intermediate Remote application (over 400 MW) and DoD is implementing this technology at numerous DoD sites in direct support of operational readiness. Five examples are: Grasmere Range, Mountain Home AFB, Idaho; Range Electronic Warfare Simulator, San Clemente Island, California, isolated from the island grid; Junction Ranch Radar Cross Section Test Complex, China Lake CA; Wild Horse Mesa Radar Facility, China Lake, California; Tank Target Range at Marine Corps Air Ground Combat Center, Twenty-nine Palms, California.

Totally these systems are reducing carbon dioxide emissions by 287 tons per year, nitrogen oxide by 12,955 pounds per year, sulfur oxide by 233 pounds per year. Fuel savings is 113 thousand gallons per year. This technology also has direct application to other public and private Organizations including the National Park Service, Southern California Edison, Arizona Public Service, and Idaho Power.

Solar Dish/Stirling - A Remote Power Source - Fort Huachuca will soon use energy from the sun to help power a small portion of the southern Arizona military post using renewable-energy technologies sponsored by SERDP and enhanced at Sandia National Laboratories in partnership with industry. A prototype dish-Stirling solar system, which consists of a large dish of solar concentrators and a Stirling heat engine, has been installed at Fort Huachuca and should be in operation by the end of August. The system will provide 7 kilowatts (KW) of electricity, or about 1 percent of the electricity currently used to power the Joint Interoperability Test Command's (JITC) 93,000 square foot main testing building. Field operation of the dish-Stirling system will help to determine its effectiveness and potential for commercialization on the world market and at other military posts.

Major Global Environmental Change Accomplishments:

First Ever UAV Measurements of Flux Profiles Under Clear Sky Conditions - The interaction of clouds with the Earth's solar and thermal radiation within the troposphere is not sufficiently understood for current global models to accurately portray the influence of clouds on global warming and cooling. Lacking the observational data to provide this understanding, climate modelers have been forced to use simple models to approximate the complex life cycle of clouds and their interactions with sunlight and the earth's thermal radiation. Uncertainties in these approximations account for much of the (factor of three) range in the predicted temperature rise associated with a doubling of CO_2 (i.e., 1.5^{O} C - 4.5^{O} C). Under SERDP funding, researchers are using unmanned aerospace vehicles (UAVs) to obtain direct, airborne measurements of a number of critical radiative parameters. These data will enable scientists to test and validate tropospheric transfer models as well as to calibrate satellite-derived fluxes. This in turn will enable climate modelers to use the vast amount of existing satellite weather data to dramatically improve global climate models. Led by Dr. John Vitko of Sandia National Laboratories, an outstanding team of DOE, NASA, and university scientists have successfully completed eight UAV test flights over the Southern Great Plains Cloud and Radiation Testbed (CART) site in Oklahoma using a Gnat 750–45 UAV that was developed and operated by General Atomics. Attaining altitudes of up to 7 km, five of these flights provided the first ever UAV measurements of flux profiles under clear sky conditions.

Successfully measuring accurate and unambiguous radiative flux divergence profiles in the clear atmosphere broke new scientific ground.

SERDP Supports First Ever Verified Measurements of Formation and Decay of Antarctic Ozone Hole - An outstanding research team at the Naval Research Laboratory has developed unique, new sensors for monitoring the ozone layer, as well as atmospheric levels of chemical compounds that are important in ozone cycle photochemistry, e.g. ClO, OH, NO. These new sensors were designed for deployment aboard satellites or space shuttles. One of this family of sensors the Polar Ozone and Aerosol Monitor (POAM), provided previously unattainable data on Antarctic ozone hole formation and its regeneration for 1993 and 1995. These POAM data included over 1,000 measurements of the spatial distribution of ozone, aerosols, nitrogen dioxide, and water vapor in the Antarctic stratosphere, providing unprecedented vertical resolution of ozone layer dynamics. Navy scientists have recently validated their initial measurements of the Antarctic ozone cycle, and have performed a detailed analysis of the Antarctic ozone vortex. Data on the 1994 ozone hole seems to indicate that the hole itself was smaller and pushed more towards one side of the Antarctic polar region than was the 1993 ozone hole. However, minimum ozone values for the 1993 hole versus the 1994 hole were comparable. Analysis of the 1995 hole, which has recently reached its annual minimum, are still continuing but show that this was an unusual year. The onset and development of the Antarctic ozone hole was significantly different from 1993 and 1994 although the ultimate depletion may be similar.

Global Biomass Burning - Natural and human caused biomass burning including forest fires account for 20-40% of the ongoing world-wide buildup of greenhouse gases in the atmosphere. SERDP has supported the development of a system for the global monitoring of these fires using one of the seven sensors of the Defense Meteorological Satellite Program (DMSP). Satellite observations provide the only means for tracking global carbon emissions form fires. This system is superior to civil sensors because the positional stability of the DMSP platform provides very accurate location of the fires, outstanding resolution and daily global coverage without relying on foreign receiving stations.

The initial fire detection and location algorithms were recently completed by NOAA's National Geophysical Data Center. The United States Department of Agriculture Forest Service (USDA FS) Fire Research Laboratory is developing the fire modeling system to estimate greenhouse gas emissions form the DMSP fire observations. In addition, the USDA FS wants to test the feasibility of using the data for early detection of fires in the western US, as an aid in fire suppression. This testing will be performed during the summer of 1995 using data from the DMSP direct readout station near Sacramento, CA. The U.S. currently spends $500M annually fighting fires and sustains even larger losses in property plus some loss of human life.

SERDP Supports Breakthrough in Measuring Temperature Changes in the World's Oceans - With SERDP support, a world renowned research team lead by Dr. Walter Munk of Scripps Institution of Oceanography, validated the concept that the heat content of oceans can be measured, using acoustic transmissions, with the precision and accuracy necessary to detect global climate change (1 second time difference in acoustic transmission travel time over 5,000km=0.1°C change in heat content). This breakthrough research will: enhance global ocean model validation; provide new understanding of ocean structure; and determine the impact of global ocean variability.

Advances in low frequency source manufacturing technologies has provided the cost reduction, reliability and system performance needed for long-term ocean data collection programs. With this data, development and application of coupled ocean/atmospheric modeling and prediction systems will lead to practical applications, such as better prediction of "El Nino" effects throughout the Pacific with

recommendations on minimizing the economic impact. Results will improve the Navy's understanding of basin scale variability and the resultant effects on passive acoustic coherent signal processing in littoral areas.

A major benefit will be improved methods for merging acoustic thermometry data with existing remote sensing (satellite) ocean data bases will enable research where horizontal and depth resolution are key variables. Additionally, the international community benefits from the comprehensive marine mammal monitoring research which provides benchmark scientific data never before available on the impacts of low frequency sound on marine mammal behavior, to aid in setting better, environmentally safe criteria for noise in the sea.

Major Pollution Prevention Accomplishments:

Carbon Aerogel Potential Cost Competitive Desalination Technology - The development of carbon aerogel capacitive deionization as an alternative to waste water treatment processes such as ion exchange under the Strategic Environmental Research and Development Program may also provide a more energy efficient means of desalinating water. The monolithic aerogels provide a very high surface-to-volume ratio as well as extremely low electrical resistivity and make it possible to apply flow-through capacitors with very low pressure drop to waste water treatment. Small-scale commercial applications may be available in 3-5 years with large-scale systems may be developed in the 10-20 year time frame.

Aerogel Process Technology has been selected to receive the prestigious R&D 100 Award sponsored by R&D Magazine. This technology, which was developed by the Lawrence Livermore National Laboratory under a SERDP project, makes use of scientific breakthroughs from highly classified research during the Cold War. Carbon aerogel has an enormously high surface-to-volume ratio and extremely low electrical resistivity which are the keys that allows carbon aerogel electrodes to economically separate ions from solution. As a result the economical treatment of liquid hazardous waste streams becomes feasible with a potential dual use application for desalination. The process was developed as an electrically-regenerated alternative to ion exchange, which unlike ion exchange, guarantees no chemical secondary waste. This is especially important when treating radioactive wastes. The R&D 100 Awards, considered the Oscars of scientific invention, are an annual award to the 100 best high-technology, commercialized or commercializable technological breakthroughs. Demonstration of the carbon aerogel technology on a DoD hazardous waste stream will be accomplished in FY96.

New DoD Paint Stripping Technology - The primary method that DoD has used for many years to remove paints from aircraft and ships requires methylene chloride based stripping compounds. These compounds contain hazardous air pollutants that will be banned by Federal law by the year 1997. Under the partial sponsorship of the Strategic Environmental Research and Development Program, the Air Force's Wright Laboratory, Oklahoma City Air Logistics Center, and Pratt and Whitney is developing a Large Aircraft Robotic Paint Stripping System (known as LARPS) that replaces manual chemical stripping. The high pressure water process has been successfully tested and is approved for future use on numerous military aircraft and reduces hazardous waste by over 90%, eliminating 135,000 gallons of chemical strippers per year at the Oklahoma City Air Logistics Center alone. Using the same technology, the Navy developed and demonstrated a system for stripping paint from ships and submarines in dry docks. The system is presently being considered for use by the commercial shipping industry.

Laser Ignition Reduces Hazardous Components from Ordnance and Provides More Firepower - The ignition train for all DoD guns consists of a series of highly sensitive primers and igniter materials.

Millions of pounds of these environmentally hazardous materials are manufactured, transported, inventoried, and stockpiled each year and, eventually, destroyed if not used within the specified time. Together, the U.S. Army Research Laboratory (ARL), the Armaments Research Development and Engineering Center (ARDEC) and Benet Laboratories have developed a Laser Ignition System (LIS) for guns which utilizes light to replace chemical ordnance ignition materials.

LIS has the dual advantages of providing significantly increased rates of fire while completely eliminating all primer and igniter materials. The LIS is completely compatible with all currently fielded artillery propellant charges as well as the developmental Modular Artillery Charge System. Under partial SERDP sponsorship, ARL has performed fundamental investigations of the interaction of laser light with propellants to determine the optimum wavelength, pulse duration and energy threshold for reliable ignition. Leveraged SERDP and PM funding, and technological developments from 8 ongoing ARL Small Business Innovation Research projects and 2 Cooperative Research Development Agreements, supported basic research that lead to a recent completely successful demonstration of this technology in the Army's Paladin M109A6 self-propelled howitzer for the U.S. Army Field Artillery School, Ft. Sill, OK. SERDP has helped support the development of a technology that will allow for eventual elimination of millions of pounds of hazardous materials per year while providing substantial mission enhancing performance benefits.

DoD Next Generation Fire Suppression - While powerful fire suppressants, Halons cause ozone depletion and national and international legislation has dictated its phase-out. The Montreal Protocol on Substances that Deplete the Ozone Layer and the Copenhagen Amendment accelerated required production phase-out in 1994. DoD currently relies on a Halon bank to meet existing needs. A new class of fire suppressants, known generally as solid particulate aerosols (SPA), is being developed in a variety of private and public sector programs. SPA's have very high volumetric efficiency, low initial and life cycle costs, low toxicity, and no known global atmospheric environmental impacts. Preliminary indications are that these aerosols are up to six times more powerful as fire suppressants than Halon on a mass basis. Potential applications include: facilities, aircraft cargo containers, portable rapid deployment shelters, fuel storage tanks, battery rooms, unmanned telecommunications facilities, and armored vehicle engine compartments.

The speed of aerosol formation depends on system design. This highly leveraged SERDP effort is focusing on testing the effectiveness of SPA's against Class A, B, C, and D fires. It is investigating the thermal characteristics of SPA materials, methods and materials for absorbing the thermal output of combusting SPA, aerosol cooling techniques and flame suppression methods. Results should include new applications such as fire protection systems that can be easily built into deployable shelters, hand thrown and remotely launched devices that can be used to provide the first steps in the process of extinguishment, and the potential to protect large fuel storage tanks with very compact fire suppression systems.

Clean Agile Manufacturing Reduces Reject Rate - Clean Agile Manufacturing for Energetics (CAME), a project of the Strategic Environmental Research and Development Program, has demonstrated a 5-fold reduction in the rejection rate during loading of BLU-97 sub-munitions (used in both the Joint Stand-Off Weapon and the Tomahawk Missile). A momentum transport problem which caused underloading of the bomblets was eliminated by using smart process control to track the volumetric flow rate as a function of ram velocity and to track shear stress as a function of applied pressure. As a result, the rejection rate was reduced from 24% to 5%. Additional refinements are expected to reduce the rejection rate to near zero.

In a related development, the CAME also demonstrated a new manufacturing process for the experimental DoD explosive TNAZ at the 20 Kg scale. The process eliminates the use of chlorinated and ozone depleting solvents during manufacture. This demonstration confirmed earlier results of a 10-gram demonstration. In addition to eliminating chlorinated and ozone depleting solvents, the process increases the yield from the manufacturing process by a factor of five; from 15% to 75%.

Changes in Military Specifications

Military specification changes resulting from SERDP efforts are highlighted in Table I. All specification changes are a result of progress made in the area of Pollution Prevention and address metal working/coatings applications.

TABLE I
Changes in Military Specifications

NUMBER	PROJECT	SPEC #	CHANGE
PP-67	Solvent Substitution and Low VOC Cleaners	MIL-C-85704	Revised to include a low VOC type turbine engine cleaner to replace the high solvent (methylene chloride) type. Two products were qualified.
PP-65	Organic Protective Coatings and Application Technology High Solids Epoxy Primer	MIL-P-23377	Addition of Non-Chromate Primer Class (N) to meet proposed Clean Air Act rule. Demonstration of this technology is in progress and will continue in FY96. Spec was also revised to eliminate all non-VOC compliant classes and all ODS chemicals.
PP-65	Organic Protective Coatings and Application Technology Water-borne Epoxy Primer	MIL-P-85582	Addition of Non-Chromate Primer Class (N) to meet proposed Clean Air Act rule. Tech Demo on-going. One material qualified to non-Chromate class. Spec also revised to eliminate all non-VOC compliant classes and all ODS chemicals.
PP-65	Organic Protective Coatings and Application Technology Touch-up Lacquer Coating	MIL-C-81352	Addition of a Water-borne Polyurethane Class (II) to provide a low VOC one-component touch-up coating to meet proposed Clean Air Act CTG limits. Service demo of two materials in progress.
PP-65	Organic Protective Coatings and Application Technology Elastomeric Primer	TT-P-2760	Addition of Non-Chromate Primer Class (N) to meet proposed Clean Air Act rule.

TABLE I Changes in Military Specifications			
PP-66	Aircraft Maintenance Chromium Replacement Anodize Process	MIL-A-8625	Revised to include both Sulfuric/Boric Acid (IC) and Thin Film Sulfuric Acid (IIB) types as alternatives to Chromic Acid Anodizing to meet proposed Clean Air rule. Technology has been implemented at NADEP North Island, and is in progress at the other Depots. Transition to entire Aerospace industry via the spec revision.

Recommendations or Proposals to Congress

There are no recommendations at this time.

FY 1995 Program

In FY 1995, 97 projects were funded from the $61.9 million appropriation.

A summary of the FY 1995 Program funding distribution by Technology Thrust Area is shown in **Table II.** **Tables III through VIII** show titles, executing organizations and actual FY 1995 funding received by the projects. Those projects not described in the *Five-Year (1996-2000) Strategic Investment Plan* section of this document may be found in the *SERDP FY 1995 Annual Report and Five Year (FY 1995-1999) Strategic Investment Plan* published in August 1995.

TABLE II FY 1995 FUNDING SUMMARY	FY 95 Funding $(K)
Cleanup	13,952
Compliance	7,185
Conservation	3,050
Energy Conservation/Renewable Resources	2,470
Global Environmental Change	16,815
Pollution Prevention	7,060
FY 1995 Scientific Advisory Board and Council Support	1,808
Undistributed Reductions	9,567
FY 1995 APPROPRIATION TOTAL	**61,907**

TABLE III FY 1995 CLEANUP PROJECTS	Actual Funding FY 1995 $(K)
Characterization, Monitoring, Modeling, Measurement, Methods - Field	
Accelerated Tri-Services SCAPS Sensor Development (A/AF/N)	1,120
The Sensitive Detection of Unexploded Ordnance and other Hazardous Materials (A)	94
Field Portable FTS Fiber Optic VOC Sensor (AF)	150
In-Situ "Inside-Out" Nuclear Magnetic Resonance Sensor for Contaminant Identification (N)	200
Integrated Characterization Program Combining DOE UFA and DoD Sensor Technologies (DOE/N)	100
Subsurface Gas Flowmeter (DOE)	100
Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation (EPA/N)	250
Subsurface Bioremediation Process Monitoring Indicators (EPA)	200
UXO Detection Feasibility Study (A/N/AF/DOE)	100
Mobile Underwater Debris Survey System (N)	575
Natural Attenuation of Explosives Contaminants (A)	100
Rapid Detection of Explosives and Other Pollutants (N)	125
Hazard Risk Assessment, Modeling, Methodologies	
Trichloroethylene Risk Assessment (AF/EPA)	0
Treatment Technologies - Groundwater/Surface Water	
Biosorption Treatment of Plasticizers and Solvents (A)	243
Enhancing Bioremediation Processes in Cold Regions (A)	220
Peroxone Treatment of Contaminated Groundwaters (A)	180
Aerobic Bioremediation of a Contaminated Aquifer (AF)	600
Bioremediation of Hydrazine/Energetic Materials (AF/A)	0

TABLE III FY 1995 CLEANUP PROJECTS	Actual Funding FY 1995 $(K)
Catalytic In Situ Treatment of Chlorinated Solvents (AF/EPA)	0
Joint US/Germany In-Situ Bioremediation Demonstration (AF)	200
Aquifer Restoration by Enhanced Source Removal (EPA/AF)	860
Removal and Encapsulation of Heavy Metals from Ground Water (EPA/DOE/A)	100
Encapsulated Bacteria for In Situ PAH Bioremediation (N)	0
In Situ Bioremediation of Fuel and Efficacy Monitoring (N/EPA)	850
Treatment Technologies - Soils/Sludges	
Air Sparging and In-Situ Bioremediation Research (A/USGS)	271
Explosives Conjugation Products in Remediation Matrices (A)	496
Integrated Biotreatment Research Program: From Flask to Field (A)	1,101
Surfactant-Enhanced Biodegradation of Contaminants (A)	234
Fuel Hydrocarbon Remediation (N)	280
DoD National Environmental Technology Demonstration Program	
Volunteer Army Ammunition Plant (VAAP) - Chattanooga, TN (A)	350
Naval Construction Battalion Center (NCBC) - Port Hueneme, CA (N)	900
Dover AFB Groundwater Remediation Field Lab - Dover, DE (AF)	1,137
McClellan AFB - Sacramento, CA (AF)	206
National Center for Integrated Bioremediation R&D Wurtsmith AFB - Oscoda, MI (EPA)	2,580
Site Characterization Consortium (EPA)	20
Cleanup Total	13,952

TABLE IV FY 1995 COMPLIANCE PROJECTS	Actual Funding FY 1995 $(K)
Boiler/Engine Emissions	
Evaluation of Metal Perovskite Catalysts for Nox Reduction (AF)	25
Compact, Closed-Loop Controlled Waste Incineration (N)	300
Reduction of Nox Emissions from Marine Power Plants (N/EPA)	300
General Hazardous Waste Management	
Lead-Based Paint Hazard Mitigation (A)	400
Emission Reduction Planning Model (AF)	100
Laser Ablation/Ionization Characterization of Solids (DOE)	100
Vapor Permeation VOC Recovery from Refueling and Storage (EPA/N)	100
Monitoring	
Advanced Mass Spectrometry for Atmospheric Monitoring (AF)	150
Leak Location in Underground Pipelines (EPA/A/N/NSF)	800
Noise Impacts	
Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness (A)	325
Open Burning/Open Detonation	
Characterization Open Burning/Open Detonation Emissions (A)	3,000
Measuring and Modeling for OB/OD Permitting (EPA)	550
Physical Treatment Processes	
Encapsulation of Hazardous Ions in Smectite Clays (DOE)	200
Kinetics of Supercritical Water Oxidation (DOE)	300
Waste Forms Based on Separations Media (DOE)	100

TABLE IV FY 1995 COMPLIANCE PROJECTS	Actual Funding FY 1995 $(K)
Shipboard Emissions	
Shipboard Non-Oily Wastewater Treatment System (N)	250
Waste Minimization/Recycling	
Evaluation of the Use of Waste Energetics as Supplemental Fuels (A/N/DOE)	185
Compliance Total	7,185

TABLE V FY 1995 CONSERVATION PROJECTS	Actual Funding FY95 $(K)
Community Ecosystem - Management	
Terrain Modeling and Soil Erosion Simulation (A)	195
Phased Array Ultrasonic Detection of Cultural Artifacts (A)	120
Advanced Biotelemetry for Resource Management (A)	270
Strategic Natural Resource Management Methodology (DOE/A)	50
Multiple - Risk/Impact Assessment	
Assessment and Management of Risks to Biodiversity and Habitat (EPA)	100
Species/Genetic - Management	
Threatened, Endangered and Sensitive Resources (A)	300
Species/Genetic - Resource Characterization	
Integration of Radiotelemetry, Remote Sensing and GIS (DOE)	50
Fishing Enforcement/Whale Monitoring Using IUSS (N/NOAA)	1,625
Species/Genetic - Risk/Impact Assessment	
The Effects of Aircraft Overflights on Birds of Prey (AF)	80
Genetic Diversity Monitoring in Plants and Wildlife (EPA)	0
Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (EPA)	0
Watershed/Landscape - Management	
Ecological Modeling for Military Land Use Decision Support (DOE/A)	260
Conservation Total	**3,050**

TABLE VI FY 1995 ENERGY CONSERVATION/RENEWABLE RESOURCES PROJECTS	Actual Funding FY95 $(K)
Energy Conservation	
Low Energy Model Installation Program (A/DOE)	500
Natural Gas Based Air Conditioning Demonstration (A/N)	270
Renewable Energy	
Fuel Cells for Military Applications (A)	150
Geothermal Space Conditioning for Large DoD Buildings (DOE)	100
Utilization of Biomass Technologies on Military Installations (EPA)	580
Photovoltaics for Military Applications (N/DOE/EPA)	870
Energy Conservation/Renewable Resources Total	**2,470**

TABLE VII FY 1995 GLOBAL ENVIRONMENTAL CHANGE PROJECTS	Actual Funding FY95 $(K)
Atmospheric Research	
Atmospheric Remote Sensing and Assessment Program (ARSAP) (DOE/N)	13,115
Ocean Research	
Acoustic Monitoring of Global Ocean Climate (ARPA)	3,700
Global Environmental Change Total	**16,815**

TABLE VIII FY 1995 POLLUTION PREVENTION PROJECTS	Actual Funding FY95 $(K)
Paint Stripping/Coatings	
Life Cycle Engineering and Design Program (EPA)	170
Organic Protective Coatings and Application Technology (N)	248
Fluorinated Ship-Hull Coatings for Non-Polluting Control (N)	414
Aircraft Depainting Technology (N)	428
High-Performance, Lead-Free Electrical Sealants (DOE/AF/N)	126
Solvent Substitution and Low VOC Cleaners (N)	99
Laser Cleaning and Coatings Removal (AF)	0
Large Area Powder Coating (AF)	0
Large Aircraft Robotic Paint Stripping (LARPS) (AF)	223
Advanced Material/Processes	
Rapid Testing for Acceptable Materials and Processes (AF)	118
Model for Facilities Life Cycle Decisions (EPA/A)	135
Other Hazardous Wastes	
Capacitive Deionization for Elimination of Wastes (DOE)	300
Acid Recycle (DOE)	169
Recycle Boiler Nitrite Solution (N)	68
Integrated Expert Solvent Substitution Data Base (EPA)	0

TABLE VIII FY 1995 POLLUTION PREVENTION PROJECTS	Actual Funding FY95 $(K)
Metal Working Process	
Alternate Electroplating Technology (N)	248
Solid State Metal Cleaning (AF)	100
Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys (A)	68
Aircraft Maintenance Chromium Replacement (N)	158
Non-Chemical Surface Preparation (AF)	274
Recycling/Purification of Plating/Cleaning Baths (N/AF/EPA)	360
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)	218
Ordnance Materials and Processing	
Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion (A)	313
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)	248
Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents (A)	158
Non Ozone Depleting Sealants for Ammunition Applications (A)	113
Solventless Manufacture of Propellants using Thermoplastic Elastomer Binder (N)	0
DoD/DOE Clean Agile Manufacturing of Energetic Materials (N/DOE)	600
Solventless Pyrotechnic Manufacturing (N)	273
Fire/Explosion Suppression	
Encapsulated Micron Aerosol Fire Suppression Technology (AF)	284
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A/NIST)	203
Chemistry of Halon Substitutes (A)	200
Advanced Streaming Agent (AF)	383

TABLE VIII FY 1995 POLLUTION PREVENTION PROJECTS	Actual Funding FY95 $(K)
Refrigerants	
Non-Ozone Depleting Refrigerants for Navy Chillers (EPA)	125
Replacements of Hydrochlorfluorocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs) (A)	236
Pollution Prevention Total	**7,060**

STRATEGIC INVESTMENT PLAN

SERDP Goals

The Departments' matters of environmental concern may be stated in terms of operational and other cost impacts to their primary missions that are necessary to meet environmental obligations, and identify those obligations that cause the greatest impact. SERDP has been implemented to minimize or remove major negative environmental impacts on the Departments accomplishing their primary missions. In doing so, SERDP supports activities relevant to the DoD mission, as well as those mission-related activities that address problems which are common to both DoD and DOE.

As the DoD's Corporate environmental S&T Program, SERDP's goals are to:

- Address environmental matters of concern to enhance military operations, improve military systems effectiveness, and help ensure the safety of personnel.
- Address defense concerns for reducing operational and life-cycle costs, including those associated with environmental cleanup and costs of full compliance with environmental laws and regulations.

In the course of addressing DoD's highest priority environmental needs, SERDP will undoubtedly help solve other significant national and international environmental problems, including the application of DoD's technical capabilities, analytical systems and information.

SERDP's goals are achieved through:

- Identifying and supporting programs of basic and applied research and development;
  - to facilitating environmental compliance, remediation, and restoration activities;
  - to minimize waste generation, including reduction at the source; and
  - to substitute use of non-hazardous, non-toxic, non-polluting, and other environmentally sound materials and substances.
- Promoting the effective exchange of information, regarding environmentally related research and development activities.
- Ensuring that SERDP R&D activities under the SERDP complement, but do not duplicate tri-service Reliance and other ongoing activities.
- Providing for appropriate access to data under the control of, or otherwise available to, the Departments of Defense and Energy that is relevant to environmental matters.

- Providing for the identification and support of research, development and application of technologies developed for national defense purposes that may address DoD matters of environmental concern.
- Conducting joint research and development projects relating to innovative technologies, management practices and other approaches.

SERDP Technical Strategy

SERDP pursues six avenues in planning and executing mission relevant defense environmental R&D:
1. Identify and fund major-impact multi-service environmental R&D programs to solve priority mission related readiness concerns of the DoD.
2. Identify opportunities to accelerate existing defense environmental quality R&D programs, and fund those that address the priority concerns of the Departments.
3. Identify, leverage adapt and/or adopt existing technologies to address environmental concerns of DoD and DOE.
4. Advance and use state of art modeling and simulation capabilities applicable to accomplish SERDP goals.
5. Use the Departments' technical and research capabilities, including, where applicable, their unique data collection and analysis capabilities.
6. Plan for a transition of successfully proven technologies to demonstration and validation.

Technical Thrust Areas

In executing this strategy, SERDP has used the existing four pillars as stated within the Services' Environmental Quality Technology Strategic Plan - Cleanup, Compliance, Conservation, and Pollution Prevention - and has historically included two additional areas - Global Environmental Change and Energy Conservation/Renewable Resources. Energy Conservation/Renewable Resources was completed in FY 1995, and work in the Global Environmental Change Thrust Area will be completed in FY 1996. Individual requirements, goals and R&D objectives have been developed for each of the five remaining SERDP Technology Thrust Areas.

The technical focus for the five Thrust Areas described in the following sections provides the direction for SERDP activities being conducted by the DoD, DOE, EPA, and other associated organizations involved in the Program.

Cleanup

This Technology Thrust Area focuses on conducting R&D to achieve more efficient and effective environmental cleanup of soil, sediment, groundwater, surface water and structures already contaminated by past practices with hazardous materials (including unexploded ordnance), radioactive (low-level or mixed wastes) and toxic substances. The principal focus of this area is more cost-effective: cleanup/remediation techniques and technologies, monitoring and characterization methods and technologies, and assessment methods.

The Departments of Defense and Energy own and operate thousands of installations, ranging from training bases to industrial production facilities. Many of the defense facilities have been operating for over a century. During this time, the agencies, like much of American society, operated them without full respect for the environment. As a result, the defense agencies now have more than 17,000 sites that require environmental cleanup. Using today's technology, the cost to remediate DoD sites alone is estimated at $35 billion, and the total cost of cleanup at current and former defense sites (including DOE sites) is projected to exceed $200 billion.

DoD and DOE need technology to reduce remediation costs, quicken the pace of cleanup, and protect human health and the environment. Experience with past environmental technology development has demonstrated a return on investment from a factor of 10 to 1000. The government must take advantage of these high returns on R&D investment and implement new innovative technologies.

The Departments' cleanup goals are: (1) to attend to imminent threats to public health and safety, (2) to remediate defense sites having a significant public health risk as quickly as feasible within the constraints of available resources, and 3) to expedite transfer of BRAC sites to future owners. In support of this goal, the site remediation objective is to provide project managers with products that will enable the initiation and/or completion of cost effective, timely remediation requirements from the user that focus on assessment, characterization, and treatment in coordination with R&D activities that support those requirements.

Within the Cleanup Technology Thrust Area, the primary environmental concerns are the need to:

- Comply with various Federal and State regulations.
- Implement timely, effective, and affordable methods for site characterization.
- Ensure the use of effective, affordable remediation technologies.
- Continue development of knowledge about health and environmental effects from environmental impacts.

Cleanup Research and Development Objectives:

1. Develop site investigation methods and technologies that are capable of locating and characterizing wastes in a timely, cost effective, and quality manner.

2. Develop innovative, compliant remediation technologies that reduce costs for sites containing explosives, propellants, fuels, solvents, heavy metals, organic contaminants, radioactive (low-level or mixed wastes), and other inorganic contaminants.

3. Develop reliable and cost effective means to identify, assess, and remediate lands and underwater areas (inland, estuarine and marine) contaminated with unexploded ordnance.

4. Develop cost-effective, methods and tools to determine fate, transport, and effects of significant defense-related contaminants.

5. Develop risk-based modeling and simulation methods for establishing cleanup priorities and levels.

6. Facilitate transfer of cleanup technologies to field use. This includes, but is not limited to encouraging the use of the DoD/National Environmental Technology Demonstration Test Sites.

7. Implement use of national sensor assets as they provide significant added value to the above.

Compliance

This Technology Thrust Area includes research and development to support environmental monitoring, waste treatment and disposal, marine risk assessment, and environmental management not directly related to site restoration, but related to meeting current and future environmental compliance requirements. It also includes end-of-pipe recycling, i.e., waste that is recycled for other than its original purpose. Further, it addresses understanding the fate and transport of defense-related air and waste water discharges.

Both domestic and international environmental regulations affect issues ranging from control of hazardous materials and effluents, and air and water quality, to remediation methodologies. The affected defense activities and assets include training and operating installations, ordnance and weapons manufacturing, repair and rebuilding installations, and ships and aircraft.

At the international level, the International Maritime Organization's Marine Pollution Convention (MARPOL) Annexes (to which the United States subscribes) are restricting or prohibiting DoD operations in international waters and MARPOL Special Areas unless vessels meet international environmental statutes. In addition, countries that host DoD facilities are implementing and enforcing compliance with regulations and standards that restrict or prohibit DoD operations in foreign ports and bases. DoD is projected to spend between $2-3 billion annually for compliance through the year 2000. New technology must be developed to reduce this cost and enable compliance with the increasingly stringent requirements of evolving national and international regulations to fulfill its mission unencumbered by regulatory fines, restricted access, and negative public reactions.

The Departments' compliance goal is two fold: (1) to ensure that all applicable environmental rules and regulations are met; and (2) to eliminate or reduce the chances for Notices of Violation (NOVs).

The primary concerns of this thrust area have a direct relationship to losses of operational capability, costs of compliance, and significant legal requirements. These concerns are embodied within pertinent domestic legislation, and include the need to:

- Control and monitor air and waste water discharges.
- Control and monitor solid waste, including plastics processing and biodegradation for maritime and land-based uses.
- Conduct effective treatment and disposal of hazardous waste.
- Monitor and control noise generation and transport.
- Characterize pollutants and waste behavior.
- Implement compliance, monitoring, and assessment tools.

Compliance Research and Development Objectives:

1. Develop control, treatment and disposal technologies for ship operations (bilge, grey/black waste water, solid waste management and air pollution).
2. Perform research on environmentally and economically acceptable alternatives to open burning or open detonation of propellants, munitions and energetic materials.
3. Develop new control, treatment and disposal technologies for hazardous wastes resulting from manufacturing, maintenance and industrial operations.
4. Develop control, treatment and disposal technologies for installation support operations (waste, waste water, solid waste management and air pollution).
5. Develop control and monitoring techniques for non-energy related air toxic emissions to include development and testing of models to predict emissions of, and exposures to, pollutants from defense facilities and to design effective, multimedia environmental management strategies.
6. Develop management and mitigation technologies for noise pollution.
7. Develop control technologies to mitigate the impacts of inadvertent spills or discharges and facilitate expediency of cleanup efforts.
8. Develop improved monitoring, characterization and assessment tools related to environmental compliance and management. Encourage the use of national sensing assets to develop these tools.
9. Develop standardized risk assessment methods, protocols, models and data for air and waste water discharges from defense activities.

10. Implement use of DoD relevant renewable resources or energy conservation modifications to mitigate noxious air emissions.

Conservation

There is a growing need to effectively use and maintain training and testing facilities to support environmental and operational requirements. An important consideration in maintaining the use of these facilities is the management of natural resources, which often provide the realistic training environment in which to exercise and test the capabilities of the military forces. Various national statutes (such as the National Environmental Policy Act (NEPA), the Endangered Species Act (ESA), the National Historic Preservation Act (NHPA)), and local laws, regulations, and requirements provide specific stewardship direction for these training and testing areas. When use of a facility is limited due to noncompliance with applicable environmental regulations or public concern over environmental issues, management solutions that facilitate compliance and enable Commanders to maintain readiness must be available. This is a role of the Conservation Thrust Area.

Additionally, the Defense Department must effectively steward the natural resources under its direction in a proactive manner. The Department's goals are to conserve, protect, enhance, and manage the natural and cultural resources under its control in a manner consistent with its military mission, while simultaneously complying with all laws and regulations and providing optimal use of those resources. These goals include assessing, conserving, preserving, and restoring ecological resources and being responsive to cultural and natural resource concerns. By better understanding the environment in which they operate, the Department can improve its land-use decisions to promote conservation, while continuing to fulfill its military mission.

In pursuit of these goals, several concerns must be addressed; specifically our ability to:
a) adequately protect our natural and cultural resources, including conservation of wetlands, forests, threatened and endangered species, historic and archeological sites, rivers and waterways, and coastal barrier islands; b) provide access to training and testing areas for benefits such as recreation, agriculture, forestry, and multiple uses; and c) comply with NEPA and other regulations and policy statements. As a result, the Services have identified and prioritized user requirements to focus the R&D community on these specific needs. The SERDP Conservation Program has molded these prioritized requirements into the following groups of user requirements, all of which are considered high priority:

- Land Use Management
- Ecosystem/Biodiversity Management
- Threatened and Endangered Species Management
- Marine Resources Management
- Noise Impacts
- Cultural Resources Management.

These user requirements result in the following goals for Conservation:

- Protect the biological health and diversity of defense installation natural ecosystems.

- Reduce the cost of ecosystem management and rehabilitation.
- Improve assessment tools for monitoring long- and short-term effects.
- Recapture valuable testing/training lands lost as a result of conservation and stewardship issues, such as soil erosion and threatened and endangered species habitats.
- Improve protection of threatened and endangered species, including marine animals.
- Obtain natural and cultural resources baseline data.
- Improve tools for land use and ecosystem management.
- Assess noise impacts on threatened and endangered species.

Conservation Research and Development Objectives:

1. Develop standardized, cost effective methods to inventory, characterize, and monitor natural and cultural resources. Encourage the use of defense-unique data collection and assessment tools to develop these methods.
2. Develop and demonstrate methods and techniques to maximize availability of military lands in support of military missions, with minimal impact on natural and cultural resources in a manner consistent with the Services' missions and Federal environmental regulations.
3. Develop and demonstrate efficient and effective techniques to conserve and restore natural and cultural resources, particularly threatened and endangered species and the ecosystems on which they depend.
4. Develop and demonstrate computer-based models to determine the incremental and cumulative impact of military activities on natural and cultural resources, and assess effectiveness of conservation and restoration techniques.
5. Develop techniques to assess and predict the impact of military use on those critical elements of the ecosystem impacting biodiversity.
6. Develop methods, tools, guidelines, and decision support systems for implementing integrated resource management techniques.

Global Environmental Change

The SERDP authorizing language directs that the DoD/DOE technical advantage and infrastructure be employed toward understanding major environmental issues, recognizing the potential dual use application of this research. While this Thrust Area focuses on elements of Global Environmental Change (GEC) defined by the U.S. Global Change Research Program (USGCRP), it also serves to enhance our understanding of the weapons system environment.

The scientific community is responding to questions recently posed by national and international policy makers. The central goal of the USGCRP is to establish the scientific basis for national and international policy-making related to changes in the global Earth system. Responding to that charge, DoD, DOE, and EPA SERDP research objectives will focus on the need to distinguish natural changes from anthropogenic impacts over a range of scales commensurate with those questions.

A primary interest of the GEC Thrust Area is identification of national assets and capabilities that concurrently address environmental concerns of DoD/DOE and stated goals of the USGCRP. Research opportunities invited to address these concerns include:

- Integration of new and existing programs in data collection and analysis methodologies.
- Conduct fundamental studies of essential environmental processes addressing identified GEC issues.
- Environmental modeling of atmospheric, oceanographic and terrestrial phenomena at local and regional scales.

GEC Research and Development Objectives:

1. Develop innovative technologies to measure the global distribution of greenhouse gases, aerosols and ozone and to develop adaptive analysis technologies to understand the effects on the climate system.

2. Develop innovative technologies to measure, analyze and determine the impact of global climate change on ocean variability and the air-ocean interface.

3. Develop an understanding of hydrologic system response to energy and weather system changes, including how the energy regime affects the hydrologic regime (terrestrial) including water supply, navigation, water quality, flood control and ecosystem viability issues.

4. Develop an understanding of surface and marine processes and ecosystems and their relationship to GEC.

5. Develop, demonstrate and apply DoD, DOE and EPA remote sensing capabilities and technologies to support environmental change research and establish enhanced observation strategies and systems.

6. Determine and demonstrate the applicability of existing archives of classified data products and related database capabilities to understand and mitigate climate change.

7. Develop methods for analyzing and merging remote sensing and in-situ data measurements from various sources and times.

8. Develop enhanced ocean/atmospheric circulation models with the capability to forecast significant global environmental events at local and regional scales.

9. Develop numerical methods to establish efficient environmental monitoring systems at regional and global scales.

All GEC projects will be completed in FY 1996.

Pollution Prevention

This Technology Thrust Area focuses on reducing or eliminating point-source waste streams. The application of pollution prevention will positively influence the other SERDP Thrust Areas by encouraging the use of innovative technologies and practices, reducing pollutants to be managed at the source, and promoting the sustainable use of natural resources.

As defined under the Pollution Prevention Act of 1990, pollution prevention means "source reduction" and other practices that reduce or eliminate the creation of pollutants through increased efficiency in the use of raw materials including energy, water and other resources, or materials substitution. Source reduction is defined as any practice that reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment or disposal. Source reduction includes: equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of materials and improvements in housekeeping, maintenance, training, or inventory control. Source reduction does not include energy recovery, treatment, disposal, or end-of-pipe recycling if the waste is used for other than its original purpose. However, SERDP Pollution Prevention does address end-of-pipe recycling of wastes, if used for the same purpose. For example, munitions and their materials may be recycled for production of new munitions. Practices commonly described as "in-process recycling" also qualify as source reduction.

Executive Order 12856 "Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirements" states that the Federal Government should become the leader in the field of pollution prevention through the management of its facilities, its acquisition practices, and in supporting the development of innovative pollution prevention programs and technologies. The Executive Order challenges the heads of the Departments of Defense and Energy to voluntarily set goals to reduce their agency's total releases of toxic chemicals to the environment and off-site transfers of such toxic chemicals by 50 percent by December 31, 1999, to the maximum extent practicable through source reduction. Toxic chemicals are those listed in section 313(c) of the Emergency Planning and Community Right-to-Know Act (EPCRA).

The DoD and DOE have many unique functions, such as the development and operation of sophisticated weapons systems, that demand specialized, high-performance materials. Many of these materials are the same toxic chemicals that are targeted for voluntary reduction. The challenge to DoD and DOE is to find new high performance materials that are not toxic under EPCRA, or to determine innovative ways to use/control toxic chemicals in order to reduce releases and off-site transfers.

Waste minimization programs in the commercial sector have demonstrated that pollution prevention saves money. Clearly, pollution prevention, in areas not being adequately addressed by the private sector, will be a key approach for users to cost-effectively meet their environmental obligations, and improved technology is the catalyst for better pollution

prevention. Material substitutions, manufacturing process changes, inventory and stockpile controls, and adjustments to routine, daily processes will be required. Also, significant behavior and attitude changes by field commanders will be required before the Services can effectively conduct their missions in a manner that minimizes waste.

The Pollution Prevention Thrust Area is concerned with DoD's need to:

- Identify alternatives for hazardous and toxic chemicals/materials.
- Reduce the use of hazardous and toxic chemicals/materials.
- Reduce the volume and toxicity of wastes and pollutants through source reduction.
- Improve the efficiencies of mechanical and chemical systems.
- Incorporate environmental ramifications as key evaluation considerations in major system design and acquisition.
- Consider the life-cycle effects of materials and systems.

Pollution Prevention Research and Development Objectives:

Develop and/or evaluate:

1. Alternative materials and processes to replace defense uses of hazardous heavy metals and metallic compounds (e.g. chromium, cadmium, lead, nickel) used in plating, surface finishing, adhesives, and sealants.

2. Alternatives to defense uses of hazardous and toxic chemicals used for surface cleaning, degreasing and stripping.

3. Alternatives to volatile organic compound (VOC) coatings, adhesives, sealant, solvents and lubricants that are not being adequately addressed by industry.

4. Alternatives to defense uses of hazardous and toxic chemicals, especially ozone depleting substances (ODS) used in climate control, refrigeration, as solvents, and as fire-fighting agents. SERDP will focus on "next generation" ODS substitutes for fire-fighting agents.

5. On-line sensors and monitoring systems to prolong usefulness of toxic chemicals in defense operations such as plating, stripping, and mechanical maintenance.

6. Techniques to regenerate, recycle, re-use, and stockpile defense-unique toxic chemicals and materials, such as acids, metals, solvents, ODS, propellants, explosives and heavy metals within the operational process (in-process recycling).

7. Techniques to reduce secondary waste generation during environmental cleanup of DoD sites, and methods to most efficiently handle cleanup wastes through proper waste characterization and recycling.

8. Predictive models to aid in the development of environmentally sound weapon systems and platforms during concept development, design, test and evaluation, maintenance (logistics support documentation), and decommissioning.

9. Cost effective, environmentally preferable packaging and recycling approaches to reduce generation of solid waste from defense related operations.

10. DoD relevant energy-saving devices, such as renewable resources or energy conservation modifications that reduce greenhouse gas emissions.

Investment Strategy

A significant reduction in appropriated funds from $160 million in FY 1994 to $61.9 million in FY 1995 caused the SERDP Council to revise its investment strategy to more sharply focus this DoD Program on defense mission-relevant environmental issues while other Federal and non-Federal programs address environmental and other concerns that are not defense mission related.

Accordingly, the SERDP Council voted to complete the major efforts in Global Environmental Change and Energy Conservation/Renewable Resources in FY 1995 and 1996. Beginning in FY 1997 neither of these two technology Thrust Areas will be funded as separate areas. However, relevant technologies/capabilities from both these areas that contribute to the defense mission accomplishment will be used in the remaining four mission-relevant environmental technology Thrust Areas.

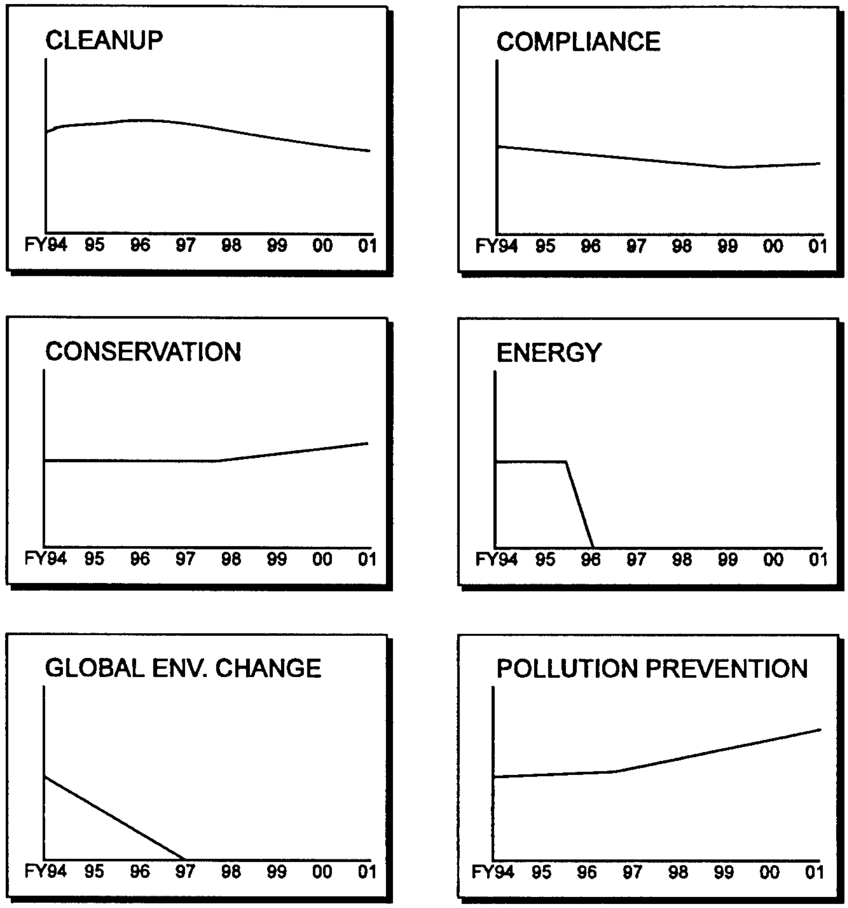
Balance Across Thrust Areas

Figure 1 conceptually depicts the anticipated relative funding trends in each of the FY 1996 technology Thrust Areas. These forecasts are based on known requirements and stated goals by the DUSD(ES). Requirements for R&D may change year to year, and, consequently, these trends may not reflect actual investment trends.

Cleanup technologies that are being developed today will be fielded in the next few years and implemented shortly after the turn of the century. DoD's goals for cleanup are targeted for completion in the following years. Hence, major impacts by SERDP on effectiveness and cost to cleanup must be brought about by currently ongoing and near-term new start projects. The investment to Cleanup is expected to decrease slightly over the next five years.

Current environmental regulations often preclude, or severely restrict, military training, operations, and manufacturing activities, if they are not in total compliance. The current regulatory environment indicates a possible decrease in environmental legislation. A commensurate slight decrease in SERDP's Compliance investment is anticipated, however this

Figure 1. Balance Across the SERDP Thrust Areas



could change with a reinvigorated environmental congressional agenda.

Conservation technologies have the potential to have the greatest impact on the readiness of military units. Research results from this area will help to resolve legal stalemates and promote environmentally sound land use management. Accordingly, investments in Conservation efforts are anticipated to increase as research efforts mature to demonstration.

The DoD is migrating from a cleanup posture to that of preventing pollution. A focused investment to eliminate future waste streams will sharply reduce or preclude the environmental consequences experienced in the past. An increase in pollution prevention technology investment is anticipated over the next five years.

FY 1996 Program

In FY 1996, 101 projects are being funded from the $58.155 million appropriation.

A summary of the FY 1996 Program funding distribution by Technology Thrust Area is shown in **Table IX**. Projects in the Global Environmental Change Thrust Areas will be completed this year.

TABLE IX FY 1996 FUNDING SUMMARY	FY 96 Funding $(K)
Cleanup	17,296
Compliance	9,584
Conservation	6,710
Global Environmental Change	2,725
Pollution Prevention	16,225
FY 1995 Scientific Advisory Board and Council Support	2,200
Undistributed Reductions	3,415
FY 1996 APPROPRIATION TOTAL	**58,155**

Table X summarizes SERDP distribution of FY 1996 funds to the Federal laboratories.

TABLE X FY 1996 FUNDING BY LABORATORY	Actual Funding FY 1996 $(K)
ARMY	
Armament Research, Development, and Engineering Center	173
Army Environmental Center	500
Army Research Laboratory - Aberdeen Proving Ground	2,153
Center for Health Promotion and Preventive Medicine	43
Cold Regions Research and Engineering Laboratory	1,029
Construction Engineering Research Laboratories	2,465
Dugway Proving Ground	1,505
Edgewood Research, Development and Engineering Center	250
Natick Research, Development and Engineering Laboratory	125
Waterways Experiment Station	4,403
ARMY LABORATORY TOTAL	**12,646**
AIR FORCE	
Armstrong Laboratory - Tyndall AFB	2,931
Armstrong Laboratory - Wright Patterson AFB	1,250
Phillips Laboratory	400
Wright Laboratory - Tyndall AFB	647
Wright Laboratory - Wright Patterson AFB	2,637
AIR FORCE LABORATORY TOTAL	**7,865**

TABLE X FY 1996 FUNDING BY LABORATORY	Actual Funding FY 1996 $(K)
NAVY	
Naval Air Warfare Center - China Lake	500
Naval Air Warfare Center - Patuxent River	1,383
Naval Command Control & Ocean Surveillance Center	1,506
Naval Facilities Engineering Service Center	1,320
Naval Research Laboratory	3,492
Naval Surface Warfare Center - Carderock	2,243
Naval Surface Warfare Center - Crane	100
Naval Surface Warfare Center - Indian Head	545
NAVY LABORATORY TOTAL	**11,089**
DEPARTMENT OF DEFENSE LABORATORY TOTAL	**31,600**
DOE	
Argonne National Laboratory	850
Brookhaven National Laboratory	100
Lawrence Livermore National Laboratory	560
Los Alamos National Laboratory	560
Oak Ridge National Laboratory	264
Pacific Northwest Laboratory	726
Sandia National Laboratory	1,585
Savannah River Technology Center	100
DOE LABORATORY TOTAL	**4,745**

TABLE X FY 1996 FUNDING BY LABORATORY	Actual Funding FY 1996 $(K)
EPA	
National Center for Environmental Research and Quality Assurance	1,800
National Exposure Research Laboratory - Athens	545
National Exposure Research Laboratory - Cincinnati	547
National Exposure Research Laboratory - Las Vegas	304
National Health and Environmental Effects Research Laboratory - Gulf Breeze	100
National Risk Management Research Laboratory - Ada	845
National Risk Management Research Laboratory - Cincinnati	935
National Risk Management Research Laboratory - Edison	25
National Risk Management Research Laboratory - Research Triangle Park	1,622
EPA LABORATORY TOTAL	**6,723**
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY	
Chemical Sciences Technology Laboratory	110
NIST LABORATORY TOTAL	**110**
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION	
Marine Mammal Laboratory	425
NOAA LABORATORY TOTAL	**425**
TOTAL FY 1996 LABORATORY FUNDING	**42,973**

TABLE X FY 1996 FUNDING BY LABORATORY		Actual Funding FY 1996 $(K)
OTHER RECIPIENTS		
Advanced Research Projects Agency		2,000
Air Force Air Logistics Command		375
Ft. Knox		10
National Science Foundation		54
Office of Naval Research		3100
US Army Corps of Engineers, Baltimore District		100
U.S. Geological Survey		298
OTHER RECIPIENTS FUNDING TOTAL		**5,937**
TOTALS		
FEDERAL LABORATORIES		43,603
DoD	31,600	
DOE	4,745	
EPA	6,723	
NIST	110	
NOAA	425	
OTHER FEDERAL RECIPIENTS		5,937
POLLUTION PREVENTION ENHANCEMENT* (Performers to be determined)		3,000
UNDISTRIBUTED REDUCTIONS		3,415
FY 1996 SCIENTIFIC ADVISORY BOARD AND COUNCIL SUPPORT		2,200
TOTAL FY 1996 SERDP FUNDING		**58,155**

*Congressional Interest Item

FY 1996 Project Descriptions

Technology Thrust Area summaries and project descriptions of the FY 1996 SERDP projects are provided in the following sections at the tabs.

TABLE XVII
FY 1996 CLEANUP PROJECTS

TABLE XVII FY 1996 CLEANUP PROJECTS	FUNDING $(K) FY96	ID Number	Page Number
Characterization, Monitoring, Modeling, Measurement, Methods - Field			
Accelerated Tri-Services SCAPS Sensor Development (A/AF/N)	2,164	729	CU-3
In-Situ "Inside-Out" NMR Sensor for Contaminant ID (N)	100	38	CU-11
Subsurface Gas Flowmeter (DOE)	275	404	CU-16
Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation (EPA/N)	250	371	CU-21
Subsurface Bioremediation Process Monitoring Indicators (EPA)	100	383	CU-27
Mobile Underwater Debris Survey System (MUDSS) (N)	730	52	CU-33
Application of Neural Network Model Coupled with Genetic Algorithms to Optimize Soil Cleanup of Subsurface Contamination (A)	196	1049	CU-39
Natural Attenuation of Explosive Contaminants	800	1050	CU-43
Rapid Detection of Explosives and Other Pollutants (N)	200	28	CU-44
Hazard Risk Assessment, Modeling, Methodologies			
Trichloroethylene Risk Assessment (AF/EPA)	900	115	CU-48
Treatment Technologies - Groundwater/Surface Water			
Biosorption Treatment of Plasticizers and Solvents (A)	600	711	CU-53
Enhancing Bioremediation Processes in Cold Regions (A)	200	712	CU-59
Peroxone Treatment of Contaminated Groundwaters (A)	496	726	CU-64
Bioremediation of Hydrazine (AF)	555	118	CU-71
Bioremediation of Energetic Materials (AF)	100	886	CU-74
Catalytic In Situ Treatment of Chlorinated Solvents (AF/EPA)	550	107	CU-77

TABLE XVII FY 1996 CLEANUP PROJECTS	FUNDING $(K) FY96	ID Number	Page Number
Joint US/Germany In-Situ Bioremediation Demonstration (AF)	200	99	CU-82
Aquifer Restoration by Enhanced Source Removal (EPA/AF)	1,100	368	CU-85
Removal and Encapsulation of Heavy Metals from Ground Water (EPA/DOE/A)	500	387	CU-90
Encapsulated Bacteria for In-Situ PAH Bioremediation (N)	500	23	CU-94
In Situ Bioremediation of Fuel and Efficacy Monitoring (N/EPA)	700	30	CU-99
Treatment Technologies - Soils/Sludges			
Air Sparging and In-Situ Bioremediation Research (A/USGS)	321	744	CU-105
Explosives Conjugation Products in Remediation Matrices (A)	200	715	CU-110
Integrated Biotreatment Research Program: From Flask to Field (A)	1,962	720	CU-114
Surfactant-Enhanced Biodegradation of Contaminants (A)	397	731	CU-122
DoD National Environmental Technology Demonstration Program			
Volunteer Army Ammunition Plant (VAAP) - Chattanooga, TN (A)	500	723	CU-129
Naval Construction Battalion Center (NCBC) - Port Hueneme, CA (N)	600	863	CU-135
Dover AFB Groundwater Remediation Field Lab - Dover, DE (AF)	621	866	CU-140
McClellan AFB - Sacremento, CA (AF)	375	861	CU-146
National Center for Integrated Bioremediation R&D Wurtsmith, AFB - Oscoda, MI (EPA)	800	864	CU-151
Site Characterization Consortium (EPA)	304	374	CU-157
Cleanup Total	17,296		

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Accelerated Tri-Services SCAPS Sensor Development

3. Agency: Army

4. Laboratory: United States Army Corps of Engineers (U.S.A.E.) Waterways Experiment Station (WES)

5. Project ID: #729

6. Problem Statement:

Currently, site characterization represents a significant portion of remediation efforts, accounting for approximately one-third of the total costs. Environmental site characterization has been traditionally based on drilling, sampling, and laboratory analysis. Complete delineation of subsurface contaminants usually requires trial-and-error placement of a significant number of monitoring wells and extensive sample collection efforts. Laboratory analysis of samples taken in the field is time consuming, costly, and often imprecise due to site history, contaminant profiles, and biogeochemical interactions. This traditional approach to site characterization hampers remediation efforts because of its uncertainty, time requirements, and cost.

The Site Characterization and Analysis Penetrometer System (SCAPS) was developed to address many of these deficiencies. SCAPS combines traditional cone penetrometer technology with contaminant and geophysical sensors to rapidly provide a profile of contaminants and geophysical properties in a cost effective manner. The SCAPS has progressed under sponsorship of the Tri-Services and DOE, and is an ideal platform for advanced sensor systems.

There exists a critical need to develop advanced sensor technologies to characterize sites containing metals, POL's, solvents, explosives, and radioactive contaminants. In order to maximize their payoff in future remediation efforts, it is critical that environmental sensors be developed and transitioned as rapidly as possible. This project addresses the need to accelerate the research, development, and demonstration of sensor, sampling, and associated data processing technologies for SCAPS.

7. Project Description:

The goal of the accelerated sensor program is to develop technologies for detecting and delineating contaminants and for characterizing geophysical properties in situ. This Tri-Service program is leveraged with supporting research sponsored by DOE and EPA. It includes a comprehensive and jointly executed set of tasks to significantly accelerate the development of

sensors for the SCAPS system. This project partially fulfills SCAPS Thrust milestones as identified in the 1994 Tri-Service Environmental Quality R&D Strategic Plan.

Under this scope of work, the Tri-Services will accelerate the development of new sensor systems that will expand the capability of the SCAPS for in situ detection of chemical contamination. Additionally, this project includes development of improved sampling, analysis, and processing technologies to support the enhanced sensor technologies. The following are the primary thrusts for this project:

<u>(1) Laser-Induced Breakdown Spectroscopy (LIBS)</u>. A fiber optic based LIBS system using pulsed laser energy to generate plasma from solid and liquid samples is being developed jointly by the DoD. Emission spectra from the plasma provides simultaneous multi-element analysis of metals including Zn, Cr, Pb, Cu, Ni and Cd. However, several technical challenges remain to be overcome before LIBS technology is viable for SCAPS implementation. This research effort includes; (a) evaluation of potential approaches for in situ generation of the plasma in the soil with the penetrometer probe, (b) characterization and optimization of the fiber optic delivery system for the laser pulse, (c) development of software techniques for detecting atomic line spectra of heavy metals, and (d) develop neural network pattern recognition schemes for processing spectral emission data.

<u>(2) Fiber Optic Raman Sensor (FORS)</u>. A prototype Raman sensor system is currently being evaluated for measurement of selected volatile aromatic hydrocarbons and solvents in soils. Technical issues include sensitivity and interferences from fluorescence components in the sample. Sensitivity enhancements will be accomplished by improvements in sensor and probe design. Wavelength shifting of the Raman excitation source will be evaluated for minimizing interferences from background fluorescence. Multiple wavelength and tunable laser sources will be developed and tested as a means of minimizing fluorescence background signals and for performing resonance enhanced Raman spectroscopy.

<u>(3) Improved Laser-Induced Fluorescence (LIF) Sensor</u>. The Tri-Services are currently evaluating new laser sources and detectors for improving the existing LIF sensors for POL contaminant detection. In order to enhance both the sensitivity and range of POL contaminants detected, the following research efforts will be conducted: (a) evaluate multiple wavelength UV sources including Raman shifters and Optical Parametric Oscillators as alternatives to the current dye lasers, and (b) increase the amount of information collected by LIF SCAPS probes including the capability to acquire complete time resolved excitation-emission matrices. Additionally, the feasibility of laser based sensors for detection of explosives in soils by photofragmentation/LIF methods will be investigated.

<u>(4) Electrochemical Sensors</u>. Electrochemical sensors for detecting volatile organic compounds (VOC) and low concentrations of explosives contaminants are currently being developed. These sensors presently require probes that provide thermal energy necessary to vaporize or desorb volatile and semi-volatile contaminants in situ for detection. Development of these probes and interfacing with electrochemical sensors will require extensive laboratory testing to fully characterize operation and robustly compare electrochemical sensor results to conventional

methods. The laboratory testing will encompass a number of soil matrices to identify and mitigate possible interference sources, and to quantify their detection limits. Subsequent development efforts may be required to improve sensor performance and overcome soil matrix effects.

(5) Spectral Gamma Probe. A SCAPS spectral gamma probe for detection of radioactive wastes is currently under development by DoD for DOE. Enhancements to the detector hardware, signal conditioning, and data processing will be made to increase sensitivity and selectivity, and to better characterize the collected emission spectra. Laboratory tests will be conducted to define and document system performance.

(6) Sampling Technology. Improved and innovative sampling technology to enhance the capability to collect soil, groundwater, and vapor samples using SCAPS will be developed. A critical issue common to all sampling technology is analyte behavior in the region of the sampler. An extensive laboratory testing program based on the multiport sampler technology previously developed will be used as a base to describe analyte behavior. Multi-port sampling technology will be developed to increase sampler range to an umbilical length of 45 meters. Analyte behavior will be related to contaminant pressure and concentration consistent with site characterization objectives, and sampler performance will be fully characterized for diverse geophysical environments. Coupling sampler technology to surface analytical instrumentation will be investigated including such methods as extraction into an inert carrier gas with an infrared heated flexible fused quartz transporter column.

(7) Data Processing Methodologies. Data acquisition, analysis, and visualization software for SCAPS will be developed to fully exploit the capabilities of the emerging sensor and sampler technologies. Developed software will include a data base management system, graphic display capability, geostatistical decision analysis, and an interface to groundwater and contaminant transport decision analysis models. The approach will be to develop a basic set of software tools which can be used to evaluate the contaminant distribution and site stratigraphy, locate subsequent sounding and sampling locations, provide a data base of all pertinent site data, and graphically display all site data in three dimensions.

(8) Technology Demonstration and Implementation. This accelerated program of sensors development will aggressively move to demonstrate the sensors on the SCAPS platform. Tri-service demonstrations, coordinated by the U.S. Army Environmental Center will be performed on VOC and improved laser-based fiber optic sensors in FY94/95. Field tests will be conducted on the fiber optic Raman sensor (FORS) in FY95.

8. Expected Payoff:

Successful completion of this work will provide the DoD and DOE an expanded scope of sensor and sampling technologies coupled with data processing and analysis software tools for SCAPS. Immediate payoff will be technology for VOC, explosives, and heavy metal contaminant detection, and improved POL detection. Improved SCAPS sampling technology will provide alternative cost effective methods to obtain site characterization and verification data. Hybrid

sampling technologies coupled to sensors and in situ methods for contaminant extraction will greatly expand the utility of SCAPS technology. The Tri-Service SCAPS will serve as a test platform for all technology development and will accelerate the evaluation of effectiveness and feasibility for subsequent demonstration activities. Rapid development of sensor technologies for SCAPS will significantly increase its return on investment (ROI).

9. Milestones/Accomplishments:

Research Area I - LIBS Sensor

1. Complete characterization of optical fiber	09/94
2. Complete laboratory prototype F.O. LIBS system	10/94
3. Complete design of prototype LIBS probe	09/95
4. Complete LIBS software development	11/95
5. Complete fabrication of LIBS prototype probe	05/96
6. Complete field tests/demonstration of LIBS system	12/96

Research Area II - LIF Sensors

A. LIF POL Sensor

1. Complete development of improved POL sensor	03/95
2. Complete field demonstrations of improved POL sensor	03/96

B. Photofragmentation/LIF Explosives Sensor

1. Demonstrate feasibility of PF/LIF for in situ explosives sensor	11/95
2. Complete prototype sensor	09/96
3. Complete field tests of explosives sensor	06/97

Research Area III - FOR Sensor

1. Complete development of laboratory FORS system	08/94
2. Complete characterization of detection capabilities	12/94
3. Complete fabrication of prototype FORS probe	03/95
4. Complete design of resonance enhanced FORS probe	09/95
5. Complete fabrication of resonance enhanced FORS probe	12/95
6. Complete FORS software development	03/96
7. Complete field demonstration of resonance enhanced FORS probe	01/97

Research Area IV - Electrochemical Sensors

1. Complete fabrication of prototype VOC and explosives sensors	09/94
2. Complete initial field test of first generation TNT sensors	09/94
3. Complete demonstration of improved electrochemical sensor systems	03/96

Research Area V - Spectral Gamma Probe

1. Complete improved SCAPS spectral gamma probe	05/95
2. Complete field testing/demonstration of improved gamma probe	12/95

Research Area VI - Sampling Technology

1. Complete initial testing of thermal desorption VOC sampler	05/95
2. Complete field evaluations of multiport VOC sampler	05/95
3. Complete laboratory testing of analyte behavior in soils	08/96
4. Complete field tests of thermal desorption VOC sampler interfaced to analytical instrument	10/96
5. Complete description of analyte behavior in soils	12/96
6. Complete evaluation of quantitative aspects of SCAPS samplers	12/96

Research Area VII - Data Processing Methodologies

1. Complete development of data processing methodology	11/94
2. Complete development of enhanced data acquisition, analysis, and visualization software	03/96
3. Complete testing and user review of enhanced software	06/96

Research Area VIII - Demonstration and Implementation

1. Complete EPA SITE demonstration of LIF POL Sensor	09/94
2. Complete initial field demonstration of electrochemical TNT sensor	10/94
3. Conduct Wurtsmith AFB, MI demonstration	06/95
4. Conduct Dover AFB demonstration	05/95
5. Complete initial field evaluation of thermal desorption VOC sampler	05/95

6. Conduct Port Hueneme, CA demonstration	06/95
7. Conduct field demonstrations of improved multiport sampler	01/96
8. Conduct demonstration of SCAPS electrochemical probes with associated software	03/96
9. Complete validated and demonstrated enhanced SCAPS LIF POL sensor and software	03/96
10. Initiate field testing/demonstration of FORS system	06/96
11. Complete demonstrations of improved sampler technologies	10/96
12. Conduct demonstrations of LIBS sensor system	12/96
13. Complete demonstrations of FORS system	01/97
14. Conduct demonstration of PF/LIF explosives sensor system	06/97

Research Area IX - Program Management

1. Conduct coordination meeting with peer review panel researchers, developers, and users	08/94
2. Conduct second coordination meeting	09/95
3. Progress report detailing first year progress	10/95
4. Progress report detailing second year progress	01/96
5. Conduct third coordination meeting	10/96
6. Final program report	10/97

To date, this project has resulted in the development and field testing of seven new SCAPS prototype probes: (a) an electrochemical sensor probe for detecting explosives in soils, (b) a fiber optic Raman sensor probe for detecting DNAPLs in soils and groundwater, (c) a thermal desorption sampler probe for detecting VOCs in soils and groundwater, (d) an electrochemical sensor probe for detecting Chlorinated solvents in soil, (e) a multiport sampler probe for collecting and analyzing subsurface liquid and gas samples, (f) an improved LIF sensor probe for detecting POL contaminants in soils and groundwater, and (g) an improved spectral gamma probe for detecting subsurface radioactive wastes. A total of five patent applications have been filed on sensors developed under this effort, and the Army has entered into two licensing agreements (Hogentogler Corp. and Applied Research Associates Corp) for commercialization of SCAPS technologies.

Newly developed SCAPS technologies have been showcased to regulators, users, and sponsors during a number of field demonstrations conducted at National Test Sites. These included demonstrations at Port Hueneme, CA involving the USEPA and the Western Governors Association, as well as demonstrations at the Volunteer Army Ammunition Plant, the Louisiana Army Ammunition Plant, Dover Air Force Base, and Wurtsmith AFB.

10. Transition Plan:

Technology developed under this project is transitioned to the Army's Environmental Center (AEC) which is the agency responsible for demonstrating and transitioning SCAPS technologies to the U.S. Army Corps of Engineers District Offices, the Naval Facilities Engineering Command, the Air Force System Program Office (HSC/YAQ), and DOE. This provides a conduit for all developed technology to DoD and DOE through a comprehensive plan that includes demonstration, documentation, training, and technical support. Transition of SCAPS technology to private industry will continue to be pursued by licensing agreements for patented technology and though Cooperative Research and Development Agreements (CRADA).

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	3,375	1,120	2,164	2,050	8,709

12. Performers:

SCAPS development is primarily a Tri-Service activity including the Army (U.S.A.E. Waterways Experiment Station, Army Environmental Center), AF (Armstrong Laboratory, AF Center for Environmental Excellence), and the Navy (NCCOSC). Additional performers include DOE, EPA, and private industry and Universities. The Loral Corp. and UNISYS Corp., under Cooperative Research and Development Agreements (CRADA) with the Air Force (AL/EQW), are involved in SCAPS LIF sensor development and demonstration. In addition, Hogentogler Corp. and Loral Corp. have a CRADA with the Navy (NCCOSC) to commercialize SCAPS LIF technologies. As part of the US/German Environmental Data Exchange Agreement we have conducted SCAPS demonstrations in Europe, and we continue to make SCAPS technologies and data available to our German partners.

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14. Keywords: SCAPS, Sensor, Environmental Sensors, Samplers, Site Characterization, Contaminant, Remediation.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** In-Situ "INSIDE-OUT" NMR Sensor for Contaminant ID

3. **Agency:** Navy

4. **Laboratory:** Naval Command, Control and Ocean Surveillance Center RDT&E Division - San Diego, CA

5. **Project ID:** #38

6. **Problem Statement:**

Determination of the feasibility for the adaptation of the emerging "INSIDE-OUT" Nuclear Magnetic Resonance (NMR) technique of compound identification to rapid site screening of hazardous waste sites. Recent developments in the area of high energy density magnets (rare earth and high temperature superconducting magnets) will allow for a significant reduction in the physical size of this type of sensor. This technique allows a well defined volume of soil surrounding the sensor to be analyzed without collection of samples.

7. **Project Description:**

The concept of reversing the locations of the sample and the source of the magnetic fields required to perform Nuclear Magnetic Resonance Spectroscopy was proposed and verified by Jackson, Burnett and Harmon[1] for the Department of Energy, Los Alamos Scientific Laboratory in 1980. The technique developed produces a region of homogeneous magnetic field external to the apparatus. A coaxial nuclear magnetic resonance coil is periodically pulsed at radio frequencies to briefly produce a toroidal magnetic field at 90° to the steady homogeneous field. If the frequency of the rf magnetic field is adjusted to synchronize or "resonate" with the Larmor frequency of precession of the nuclei present in steady magnetic field and realign the direction of their nuclear magnetization vector accordingly. The intersection of the steady homogeneous magnetic field and the toroidal rf magnetic field define the "sensitive sample volume". With the cessation of the rf magnetic pulse, the realigned or "flipped" nuclei will start to precess. The coupling between the precessing magnetization vector and the NMR coil allows the NMR free-induction decay (FID) signal to be detected. The amplitude of the signal is related to the number of nuclei present, and the rate of signal decay is related to the local environment of the nuclei, i.e., the chemical bonds to other near by atoms.

J.A. Jackson, L.J. Burnett, and J.F. Harmon, "Remote (Inside-Out) NMR. III. Detection of Nuclear Magnetic Resonance in a Remotely Produce Region of Homogeneous Magnetic Field", *Journal of Magnetic Resonance*, 41, 411-421, (1980).

Jackson[2] has demonstrated the variation of the radial magnetic field (H_r) vs. radial distance r, as a fraction of the axial magnetic field (H_0) at the center of an isolated magnet. With a h/a value of 3, where h is the axial distance from the pole face to the midplane and a is the radius of the pole face respectively, the radial magnetic field is very uniform for the region defined by the ratio r/a between the values of 1.9 - 2.8.

The Larmor frequency of the precessing magnetization is given by: $B = B_p \cos(w_0 t)$ where: B_p is the value of the radial magnetic field in the region discussed above, w_0 is the Larmor frequency, and t is time. If the quantity g is referred to as the relative signal per unit volume of toroidal sample, referenced to a known coaxial sample of volume V_r, then g can be expressed as

$$g \equiv (I_s/V_s) \,/\, (I_r/V_r) \qquad [1]$$

where I is signal amplitude and V is the volume of material involved, and the subscripts $_s$, $_r$ and $_c$, denote the toroidal and reference samples, and the NMR resonance coil respectively.

For brevity, the following simplifications will be made: R is taken to be the average of the inner and outer radii of the toroid in the mid-plane, and R >> than the radius of the cross section of the toroid. That Faraday's law for the sample coil, with a quality factor of Q and N number of turns, can be expressed as $I = -NQA(d\phi/dt)$ with $\phi = B \cdot A$ and $B = B_p \cos w_0 t$. Then, the peak value B_p for the reference sample can be expressed as $B_p = 4\pi\mu_p nf$ & $\mu_p nf = M$ where M, the magnetization, is based on the proton magnetic moment, the number density of protons, and the Boltzmann factor for the fraction of protons contributing to the net magnetization.

For the sample, only a portion of the flux is link and
$A = A_c = \pi a^2$, then $B_p = MV_s/R^3$ and
$I_s = NQA_c w_0 B_p \sin w_0 t = NQA_c w_0 [MV_s/R^3] \sin w_0 t$ so that,

$$(I_s/V_s) = NQA_c w_0 [M/R^3] \sin w_0 t \qquad [2]$$

Similar manipulation for the reference sample's value results in

$$(I_r/V_r) = 4\pi NQ w_0 M/l \sin w_0 t \qquad [3]$$

where l is the length of the reference sample and $V_r = A_r l$.

Combining Eqs. [1], [2], and [3] results in the relative signal per unit volume
$g = a^2 l/4R^3$

involving only geometric parameters of, or define by, the apparatus and the maximally coupled reference sample (the best instrumental signal that can be obtained).

J.A. Jackson, "Nuclear Magnetic Resonance Well Logging", *THE LOG ANALYST*, 16 - 30, SEPTEMBER-OCTOBER, 1984.

Substitution of practical values for these parameters, as reported by Jackson[3], for the radial magnetic field in an acceptable operating configuration (r/a = 2, a = 5 cm, reference sample length ≈ 5 cm) yields a value for g=0.05. This is in agreement with experimentally measured values of g reported by Burnett and Jackson[4] of 0.04 for this ratio of r/a. These experimental studies employed a radial magnetic field of ≈ 120 G, derived from large Alnico permanent magnets, and a Larmor frequency of ≈ 500 kHz; this produced a signal-to-noise ratio (S/N) of 1:20. Much of the noise associated with these measurements resided in the electronics used to process the signals. Modern contemporary electronics and signal processing techniques should result in an improvement of the S/N ratio, and improve the operational reliability and sensitivity.

Consultation with Prof. Lowell Burnett (a nationally recognized NMR expert, and author of the works cited above) of San Diego State University and President of Quantum Magnetics, has indicated that this proposed sensor has a high probability of success for its envisioned use, particularly for high explosive compounds and petroleum based products. He has proposed to cooperatively develop this project, manufacture and market and viable product which may evolve as part of the technology transfer effort.

8. Expected Payoff:

This detector, when fully developed, will allow for rapid and cost effective screening of proven and/or suspected sites contaminated with chemical compounds for which it has been calibrated. The ability to identify and quantify contaminants in subterranean strata behind well casings will allow the placement of a single test well, drilled and cased to the maximum investigative depth, rather than many wells which vary in depth in order to collect the necessary strata effluent. The reduction in the number of unnecessary test wells and their attendant costs in time and money, for installation, sample collection, laboratory analysis, and sample transportation, is considerable. If the number of test wells can be reduced by a factor of five (80% reduction in the number of wells), it is estimated to reduce the overall cost of this phase of site remediation approximately 40 - 50%, by accurate determination of the boundaries and depth of the contaminant plume before and after site remediation efforts.

If we conservatively estimate the cost of drilling and casing a well at $20/ft, for a 50 ft well, and disposal of the tailings, at $4,000.00; the associated required test well lifetime of analytical laboratory analysis (X samples per year for Z years as required by EPA) at $5,000.00; then the cost per well is $10,000.00. Further, assume that the time required to install a well and receive the initial laboratory analysis report (approximately 4 weeks) would not be lost. If the number of well installed per year is reduced by 500, then the monetary savings will be $5,000,000.00. Also, the environmental and personnel health risks are reduced since the amount of hazardous tailings wastes generated during the drilling operations will be reduced in proportion to the number of wells drilled.

J.A. Jackson, ibid.

9. Milestones/Accomplishments:

1. Complete assembly of laboratory NMR spectrometer system	02/96
2. Complete measurements of target compounds	08/96
3. Complete assessment of feasibility	10/96

1) Extensive computer modeling has shown that an alternative design, utilizing magnetically opposed end caps on the main magnet poles, required to generate the static, external radial magnetic field for this configuration, will yield an increase in *r* and B_o (the radius of the interogated volume and the magnetic field strength). But, this configuration produces tremendous destabilizing forces between the end caps and the main magnetic poles, which will exceed the tensile strength of the supporting material. 2) Modeling of an alternative magnet configuration developed by Schlumberger, indicated poor vertical resolution capability and a reduced volume of interrogation. 3) Therefore, the first version of the probe will be developed with the Jackson-Burnett magnet configuration, employing a non-superconducting magnet. 4) Magnetic material selection has indicated that a sintered rare earth, Neodymium-Iron-Boron with a "Maximum Energy Product" of 35×10^6 Gauss-Oersteds, will produce a factor of 3 improvement in the radial magnetic field strength over the original concept's design. This will ensure that the inner radius of the torodial "sensitive sample volume" will be entirely external to the well casings. 5) RF coil modeling is continuing, with special attention to RF ground plane locations in order to yield an increase in the RF field strength in the region of interest. 6) Preliminary probe designs are being developed and refined, based on the developed functional specifications. 7) The computer based Nuclear Magnetic Resonance (NMR) Spectrometer (the analyzer portion of the system) has been completed and is ready for delivery.

10. Transition Plan:

Under the guidance of the Technical Program Officer and Technical Program Manager, the operable system will be subject to field trials at selected DoD/DOE sites. The results of those field trials shall be reported and distributed as requested. At the conclusion of this effort the operable hardware, procured as part of this effort, shall be turned over to the identified program office within the SERDP defined lead agency. The basic technology will be transferred through the development of US government patents, and through the cooperative development with the responsible industry partner, Quantum Magnetics in the United States, along with the transfer of technology previously developed for the Department of Defense as part of this effort.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	450	200	100	380	450	1,580

12. Performers:

NCCOSC, Research, Development Test & Evaluation (RDT&E) DIV, San Diego, CA (Codes 524, 754)
Quantum Magnetic (industrial partner) San Diego, CA
San Diego State University Foundation, San Diego, CA (Contractor support and consultation with faculty)

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14. Keywords:

Nuclear Magnetic Resonance, Inside-Out NMR, Nuclear Magnetic Logging

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Subsurface Gas Flowmeter

3. **Agency:** Department of Energy

4. **Laboratory:** Sandia National Laboratories

5. **Project ID:** #404

6. **Problem Statement:**

In situ air stripping is a process for removing volatile organic compounds (VOC's) from the subsurface which is currently enjoying widespread use in the environmental restoration industry. Air stripping involves injecting and/or extracting air from the subsurface through vertical or horizontal wells penetrating the contaminated horizons. The flow of air through the subsurface results in the VOC's being volatilized and removed from the ground by the flowing air. In assessing the effectiveness, efficiency and zone of influence of this technology it is important to understand the dynamics of the gas flow in the subsurface. In a perfectly isotropic, homogeneous medium the gas would travel uniformly through the ground. In the real world, however, the transport properties of the subsurface are decidedly inhomogeneous, with the result that the gas travels along preferred, high permeability pathways. To properly evaluate the remediation process, one needs to delineate these pathways and define how broad and diffuse or narrow and constricted they are. Another important consideration when gas is being injected and/or extracted from the subsurface is the amount of interaction between the gas in the pore spaces in the vadose zone and atmospheric air. These effects have not been adequately investigated because of the difficulties involved in directly measuring air flux in soil. The proposed gas flowmeter will address these needs by providing the capability to directly measure subsurface gas flow velocities.

The gas flowmeter being proposed is an extension of a technology called the In Situ Permeable Flow Sensor which has been developed by the PI with funding from DOE's Office of Technology Development. The In Situ Permeable Flow Sensor, which measures the full 3 dimensional groundwater flow velocity at a point in a saturated permeable material, was field demonstrated during the VOC Non-Arid Integrated Demonstration at the Savannah River Site and is currently licensed to a private company for commercialization. The new gas flowmeter, while similar in many respects to the previously developed In Situ Permeable Flow Sensor, differs in several important aspects.

7. **Project Description:**

The basic principle of operation for both the groundwater and gas flow probes is that the temperature distribution on the surface of a finite length, heated cylinder, buried in a permeable flow field, is strongly influenced by the magnitude and direction of the fluid flow past the

cylinder. This concept is implemented by fabricating a cylinder approximately 75 cm long by 5 cm in diameter which consists of a thin film electrical resistance heater and an array of approximately 30 temperature sensors on the surface. The interior of the cylinder is made of a material with very low thermal conductivity so that when the heater is activated, the heat flux across the surface of the cylinder is spatially uniform. When the cylinder is buried in intimate contact with the formation, this heat flux warms the fluid-saturated sediments surrounding the probe. In the absence of any flow past the probe, the temperature distribution on the surface of the cylinder is independent of azimuth and symmetric about the vertical midpoint of the probe. The ends of the probe are warmer than the midsection because heat transfers away from the ends of a finite length heated cylinder is more efficient than from the midsection of the cylinder. If there is flow past the probe, the surface of the probe is advected around the instrument by the flowing fluid. Cooler temperatures are observed on the upstream side of the probe and warmer temperatures on the downstream side. The magnitude and direction of the full three dimensional fluid flow velocity vector are determined by inverting an equation that describes the probe surface temperature distribution as a function of the flow velocity past the probe and the thermal properties of the fluid and the fluid-saturated sediments surrounding the probe (Romero, 1995). The technology is capable of measuring groundwater flow velocities as low as 10^{-5} cm/s. Since the heat carrying capacity of a given volume of air is several orders of magnitude less than that of a similar volume of water, air flow velocities measurable by the technology will be several orders of magnitude higher than detectable groundwater flow velocities. The gas flowmeter should be capable of measuring gas flow velocities s low as about 10^{-2} cm/s.

In order to accurately measure the fluid flow velocity in the formation, complications associated with making flow measurements inside of screened or open boreholes must be avoided. This can be accomplished by designing an instrument which is emplaced directly into the ground, in intimate contact with the formation. The instrument is emplaced by using a hollow stem auger, or other similar drilling technique which introduces only a minimal disturbance to the subsurface sediments, to drill down to the depth where the measurement is to be made. The probe is then lowered down the center of the drill string and the drill string is retracted from the hole, leaving the instrument permanently buried in the ground. In water-saturated, unconsolidated sediments, the formation quickly collapses around the instrument, leaving it permanently buried in a relatively undisturbed setting. In the unsaturated sediments where the gas flowmeter will be used, it is unlikely that the borehole will collapse around the tool in a timely manner and it will be necessary to back fill the hole with the sediments that were extracted during drilling. While this deployment technique means that the relatively inexpensive instruments cannot be moved or retrieved after emplacement, the flow velocity past them can easily be monitored for extended periods (months to years) making this an excellent monitoring technology.

After installation, a data acquisition system is attached to the probe and electric power is applied to the heater. The data can be collected from the data logger either in the field, using a laptop computer, or remotely via modem and telephone (land line or cellular). If continuous 110 AC electric power is available, either from a power pole or from a generator, it is a simple matter to connect a suite of flow sensors to a network of data acquisition systems and monitor them remotely via modem for extended periods of time (months to years).

For the purpose of measuring subsurface gas flow velocity, the basic principle of operation will be implemented in two different ways. One instrument will be essentially identical to the In Situ Permeable Flow Sensor and will measure the magnitude and direction of the full three dimensional gas flow velocity vector. A second version of the technology will consist of a long, thin, solid metal heater (perhaps 1 meter long by 1 cm in diameter) equipped with a vertical array of approximately 10 temperature sensors. This design will enjoy several advantages over the first design but suffer from significant disadvantages as well. The major disadvantage is that the instrument will only be able to measure the vertical component of gas flow velocity and will be insensitive to the horizontal component. In very near surface applications, such as investigations of air flux directly across the ground surface, this limitation will probably not be important. The advantages of this design are that the instrument will be less expensive, considerably more robust mechanically, and easier to emplace compared to the 3D instrument.

A few limitations on the use of the technology should be mentioned. First of all, the instruments cannot be deployed too close to the ground surface because other manifestations of surface weather such as surface temperature oscillations and rainfall events will influence the thermal behavior of the probe. Daily temperature oscillations typically penetrate to depths of a few feet and, while corrections for their effects can be applied, they will complicate data interpretation. Longer period temperature oscillations, such as storm events and seasonal surface temperature fluctuations will also have an effect, but corrections can be calculated with greater confidence. During rainfall events, surface water which may be at a significantly different temperature than the soil around the probe, will be flushed past the probes, altering the temperature signal due to air flow past the tool. The depth to which these phenomena are important depends on the thermal, hydraulic and pneumatic properties of the medium above and surrounding the probe. While these effects will be investigated for the specific site where the probes are used, the probes should probably not be deployed at depths shallower than about 10 feet.

The way in which formation gas flow velocity is currently measured is to deploy an array of pressure transducers at different points in the formation to determine the pressure gradient at the point of interest. The product of the pressure gradient and gas permeability of the soil yields the gas flow velocity. The problem is that the gas permeability of soils is very difficult to determine with any degree of accuracy. The PI is unaware of any other techniques for direct measurement of gas flow velocity in the subsurface.

The first task will be to conduct bench scale experiments in the laboratory to verify the mathematics upon which the technique is based, develop calibration procedures and to determine the sensitivity of the proposed technology to both vertical and horizontal gas flows. The second task will be to test the probes in the field and finally to deploy them at an actual waste site where in situ air stripping is being used to remediate the contaminant.

8. Expected Payoff:

The technology has the potential to dramatically improve our understanding of the dynamics of air stripping waste remediation activities, an extremely important technology currently being used extensively, both by government and private industry, to remediate hazardous waste sites. The

availability of the gas flowmeter technology will improve the cost effectiveness of air stripping projects by providing information about the zone of influence of the process at a given site, thereby alleviating the necessity of conducting overly conservative cleanup sweeps. At sites where nutrients intended to enhance bioremediation of the contaminant are being delivered into the subsurface by gas injection, this technology can yield information migration paths of the injected nutrients in the subsurface.

9. Milestones/Accomplishments:

1.	Complete lab studies and sensitivity analysis	12/95
2.	Complete and document calibration procedures	03/96
3.	Deploy instruments at a hazardous waste site	06/96
4.	Complete data collection	12/96
5.	Complete final report on technology	03/97

When work on the project began, we built a small tank (6 inches in diameter and 5 feet high) in the laboratory, filled it with sand, deployed a prototype vertical component gas flowmeter in it and circulated are past the device (along the long axis of the tool and the tank). While temperature perturbations that could be attributed to air flow in the tank were observed, it was clear that the tank was too small; substantial temperature increases were observed at the edge of the tank. We fabricated a larger tank (4 feet in diameter and 10 feet tall) and buried it in the ground with the top of the tank flush with ground. We have conducted numerous tests in the tank but have not yet overcome several difficulties associated with the establishment of uniform gas flow through the tank. While we continue to work ok improving the results from the tank experiments and are optimistic that we will soon prevail, we are currently looking to start a field test of the 3D gas flowmeter. An instrument has been fabricated and a potential field site identified. If all goes forward as planned, it is possible that a field demonstration will occur in late January/early February 1996.

10. Transition Plan:

By the completion of the work described in this proposal, the technology will have been developed to the point of commercial viability and have been tested and demonstrated at an actual waste site. As the technology is being developed, industrial partners interested in commercializing the technology will be actively sought. S. I. E., Inc. of Fort Worth, Texas, the company which is currently commercializing the In Situ Permeable Flow Sensor, has expressed an interest in participating in the development of this technology and in commercializing it, if it proves marketable.

The ultimate users of this technology will be Environmental Restoration Departments at the various DoD and DOE facilities around the country as well as private industries. Discussions with ER representatives at the DOE Hanford Site have been very encouraging.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	125	100	275	500

12. Performers:

The work described in this proposal will be carried out by the Principal Investigator, a Senior Member of Technical Staff at Sandia National Laboratories. As mentioned above, S. I. E., Inc., has expressed an interest in participating in the development of this technology.

13. Principal Investigator:

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14. Keywords:

Gas, Flow, Flowmeter, Air-Stripping, Bioremediation, Vadose.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation

3. **Agency:** Environmental Protection Agency

4. **Laboratory:** National Risk Management Research Laboratory

5. **Project ID:** #371

6. **Problem Statement:**

Petroleum hydrocarbons, and other volatile organic compounds (VOCs), which are found to contaminate groundwater and soils, are usually treated by pump-and-treat methods, which are very time-consuming, expensive, and not very effective. We are proposing the use of pervaporation for effectively removing these hydrocarbons and VOCs from contaminated soil and groundwater (with or without using surfactants) and concentrating them by at least a thousand-fold, for economical disposal or recycle/reuse using specially designed hydrophobic membranes.

This project supports the DoD's Tri-Service Environmental Quality R&D Strategic Thrust Areas: 1.H Solvents Contaminated Groundwater, 1.I Fuels Contaminated Groundwater, and 1.L Solvents/Fuels Contaminated Soils, and will partially meet or substantially contribute to User Requirements:

- Solvents in Groundwater
- Alternatives to Pump and Treat
- Improved Treatment of Water Contaminated with Chlorinated Hydrocarbons
- Chlorinated Solvents in Groundwater Treatment
- Dissolved Fuel in Groundwater (BTEX) Treatment
- Improved Recovery of Free Petroleum, Oils, and Lubricants from Aquifers
- Improved Remediation of Groundwater Contaminated with Nonchlorinated Hydrocarbons
- Improved Remediation of Soils Contaminated with Chlorinated Solvents
- Improved Remediation of Soils Contaminated with Nonchlorinated Hydrocarbons

7. **Project Description:**

Petroleum hydrocarbons and other volatile organic compounds (together described hereafter as VOCs) form various industrial activities in both civilian and military sectors are frequently found to contaminate groundwater and soils. These VOCs typically are transportation fuels, and solvents including chlorinated organic compounds such as trichloroethylene (TCE), carbon tetrachloride, tetrachloroethane (TCA). Many of these VOCs are potential carcinogens. In groundwater the VOCs exist as non-aqueous phase liquid pools (NAPLs), which are of two types, light NAPL (LNAPL) which floats on water, and dense NAPL (DNAPL) which sinks under

water. The NAPL pools are a long-term source of contamination, as the organics slowly leaks into the aquifer water, which then is unusable for human use, and if the water discharges into a river or a lake, it poses danger to aquatic life. Soil contamination by VOC is a source for continuous air pollution and is also a source for groundwater pollution.

The technology of choice for remediating these environmental problems is the so-called pump-and-treat method, one variation of which is circulating water through the contamination area and pumping it out to a treatment stage, typically carbon adsorption, which needs to be subsequently regenerated, and the VOCs disposed of chemically. We propose to develop a simpler and more effective technology which will use the membrane pervaporation method. This method removes the VOCs from the water and concentrates it by at least a thousand-fold, which permits much more economical recovery for recycle/reuse.

In the "pump" part of the pump-and-treat process, the use of surfactants has been proposed for enhancing the removal of VOCs from the groundwater or soil matrix (surfactant flushing). While the VOCs will indeed be removed more efficiently by emulsification, the oil-water emulsion is harder to dispose of by ordinary means of bioremediation or carbon adsorption. We are proposing pervaporation as a means of breaking the emulsion while removing the VOCs from the contaminated water. The efficiency of pervaporation for VOC removal from water has already been demonstrated in several studies to be better than 99%. The use of pervaporation for breaking oil-water emulsions is protected by an invention disclosure at NRMRL-EPA.

Pervaporation works on the principle of solution diffusion, i.e. the organic compounds dissolves in the non-porous membrane, diffuses out to the permeation side, and evaporates. The energy for this evaporation is conveniently provided with the feed stream itself. In contrast to conventional membrane processes, which use porous membranes, pervaporation membranes are not akin to filtration, and are therefore less prone to mechanical fouling. For VOCs, which are hydrophobic, a hydrophobic membrane is appropriate. Either a vacuum or an inert sweep gas is employed on the permeate side of the membrane. Usually the VOCs permeate through a hydrophobic membrane, such as one made of polydimethylsiloxane or silicone, orders of magnitude faster than water, as a result of which the VOCs are highly concentrated. For instance, it is possible to concentrate a 100 ppm VOC-solution to over 10% VOC solution (or suspension).

The composition and morphology of the membranes are a key to effective use of pervaporation technology. It is best to use a thin film of the discriminating layer deposited on a highly porous support structure. In addition, NRMRL-EPA has invented specially doped membranes that enhance the selectivity by 40% or more. An invention disclosure has also been made on the use of these membranes for pervaporation.

The proposed research has four parts:

1. Use of special membranes: These membranes will be designed, fabricated and tested for their superior VOC-selectivity and transport rates. The results will be useful to predict

the opportunity for improved efficiencies offered new membranes in comparison to conventional commercially available membranes.

2. Bench-scale test: Laboratory research will be conducted to investigate the removal of VOCs from simulated ground water and surfactant-flushed VOC-solutions. Transport rates, selectivity, and separation factors will be measured for one advanced membrane system of a baseline system comprised of a commercially available membrane.

3. Mathematical modeling will be conducted to predict the design features of a prototype for a designated removal efficiency. This is a mere extension of modeling currently being done at NRMRL.

4. We will conduct a pilot demonstration of a prototype for VOC-removal from contaminated water (with or without surfactant in it). We had originally proposed to demonstrate the technology at a defense facility; however, we are now developing a proposal to test in an existing EPA pilot facility to determine potential cost savings.

All work from proof-of-concept of the removal of VOCs from VOC-emulsion in water to pilot demonstration can be completed in two years from the inception of the study, which began in January of 1995.

8. Expected Payoff:

The proposed technology will make two specific advances: (1) provide a cost-effective way of dealing with surfactant-VOC solutions, and (2) provide a boost to the use of surfactants for groundwater and soil remediation. Large savings will accrue from this practical and efficient technology.

9. Milestones/Accomplishments:

Overall Study Design

1. Complete preliminary technical plan for FY95 work and overall 2 year outline — 02/95
2. Visit Naval Facilities Engineering Science Center (NFESC) at Port Hueneme for detailed discussion of technical plan and outline - begin effort to set objectives for prototype based on emission regulations — 02/95

Laboratory Experimental Phase

3. Complete detailed experimental plan for membrane screening based on simulated organic/groundwater of interest targeted by client. Tests are to be conducted to determine transport rates, selectivity and separation factors for individual organic compounds, ie. TCE and BTEX — 07/95

4. Procure hollow fiber membrane modules and complete assembly of experimental approaches — 08/95
5. Complete laboratory experiments for screening membrane effectiveness — 01/96
6. Complete laboratory data analysis — 03/96
7. Complete model development to predict performance of the hollow fiber module — 05/96
8. Complete Phase I interim progress report — 05/96

Prototype Test Phase

9. Begin prototype design based on lab studies (use of EPA pilot unit eliminates this task) — 04/96
10. Acquire contractor for demo (use of EPA pilot unit eliminates this task) — 04/96
11. Complete test site selection — 04/96
12. Develop test plan for demo — 05/96
13. Conduct field test — 06/96
14. Complete system design model using prototype and lab test data — 08/96
15. Complete Final Report — 12/96

The bench scale apparatus and experimental protocols, including operational, sampling and analytical techniques, and a quality assurance plan for evaluation of novel and baseline commercial membranes were developed and standardized for experimental use in the laboratory. A significant number of tests have been completed to evaluate the performance of the membranes in the presence of various levels of surfactant ranging from zero to 40 times the critical micelle concentration (CMC). The results indicate that the presence of the surfactant has an effect on the overall rate of mass transfer of the VOC from the liquid to the permeate side of the membrane. Indications are that the effect is related to the boundary layer thickness, the driving force across the boundary layer, or by increasing the length of the flow path. A new test cell has been designed to permit exploration of the effects of hydrodynamic variables on the PV performance. Removal efficiencies for TCE has been measured at 80 to 90% at surfactant concentrations up to 40 times the CMC. These data are the first of their kind available for removing organic solvents form emulsions by membrane systems.

The pilot unit located at the EPA/NRMRL's Test and Evaluation Facility in Cincinnati has been completed the start-up Phase, and we are now in routine testing of the Hoechst-Celanese spiral wound membrane separation system. Baseline performance tests are completed for TCA and Toluene in water at 0 to 100 ppm. Performance tests for TCA and Toluene in water with the anionic surfactant Dowfax 8390 are underway. Initial results for removal efficiencies for TCA and Toluene have been obtained; they indicate 98 to 99% removal at surfactant concentrations below the CMC, and 80 to 90% at surfactant concentrations up to 40 times the CMC.

A considerable effort has been devoted to selection of a suitable test site. The important considerations are availability in the summer of 1996, access, permitting, and contaminants present. The OU 2 site at Hill AFB and the PPG site in Louisiana appear to be the most promising based on these criteria. We are also conducting a quick study of the potential cost savings and technical feasibility of trucking the produced waters from the selected site to the

EPA/NRMRL's Test and Evaluation Facility in Cincinnati to determine if this site would be suitable for the purpose of demonstration, avoiding the time potential delays and expenses associated with moving the pilot unit into the field.

10. Transition Plan:

The pilot demonstration was originally planned to take place at a defense site, constituting technology transfer to DoD. However, we are considering the possibility of conducting the pilot plant work at EPA's Test and Evaluation Facility of significant cost savings could be relieved. We are preparing a comparative feasibility study (in-house) on this possibility.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	280	250	250	780

The NRMRL has contributed in-kind resources to the program with $60K in FY94 and $100K and 1.3 professional man-years in FY95 for the in-house study. The in-house study, which was focused on fundamentals before receiving SERDP funding, was redirected to this high priority research project.

12. Performers:

The first three parts of the delineated research will be conducted in-house at NRMRL-EPA and by the Northeast Hazardous Substance Research Center. The demonstration will be conducted by the USEPA if done at its T&E Facility, or under contract by a membrane company based on the model prediction and laboratory results.

The Naval Facilities Engineering Science Center (NFESC), will collaborate with us in all phases of this work. The center has the lead on the site selection task. Point of Contact: Ms. Leslie Karr, Code 411, NFESC, Port Hueneme, CA 93043, Tel: 805-982-1294. The Air Force's Armstrong Laboratory Environics Directorate was contacted (Capt. Mark Smith, Tel: 904-283-6244). They will be interested in demonstrating the technology at an appropriate Air Force facility, if it is shown to be cost-effective.

13. Principal Investigator:

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14. Keywords:

Emulsion, Surfactant, Pump-and-Treat, Pervaporation, Membrane.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Subsurface Bioremediation Process Monitoring Indicators

3. **Agency:** Environmental Protection Agency

4. **Laboratory:** National Risk Management Research Laboratory (NRMRL)

5. **Project ID:** #383

6. **Problem Statement:**

The application of in-situ, active or passive bioremediation of fossil fuel contamination holds promise of achieving both detoxification and source removal of regulated compounds such as benzene, toluene, ethylbenzene and xylene (BTEX). BTEX as well as other mobile constituents of fuels and solvents are a major category of subsurface contaminant mixtures present at DoD installations. These contaminant mixtures entered the subsurface as a result of spills or releases from fuel tanks, pipelines, maintenance areas, and fire-training installations. The scope of known problems, in a variety of hydrogeologic settings, requires a systematic, cost-effective approach to monitoring the progress of bioremediation processes and plume transport. In most cases, methods applied to the detection or assessment of specific subsurface contaminant distributions in aqueous or solid matrices have been applied to long-term monitoring during remedial action operations. However, disappearance of source-related compounds from ground water alone is insufficient evidence for removal. Reliable indicators of the progress of bioremediation actions, including the monitoring of metabolic intermediates in aquifer solids and water are needed in order to evaluate the performance of remediation schemes and to complement source contaminant monitoring efforts. (National Research Council, In-Situ Bioremediation When Does It Work?, National Academy Press, 1993.)

The major problem we intend to address is the need to identify biochemical pathway metabolites and critical substrates so that engineered mass-balances can be approached. In this way it may be possible to link net contaminant destruction or transformation to both hydrogeochemical conditions and specific biodegradation pathways. With this process level understanding, we should be able to more easily apply bioremediation to other sites. Acceptance of passive or "low-technology" bioremediation schemes can be achieved when mass-balances and definable endpoints for contaminant removal are achieved.

The needs for these monitoring improvements are recognized in several SERDP Thrust Areas: 1.B: Site Characterization and Analysis Penetrometer System, 1.III.1.e. Improved Standards and Analytical Techniques for Defining "Clean"; 1.C: Characterization/Monitoring, 1.III.3.a. Improved Subsurface Condition Description and Simulation; 1.D: Chemical Analytical Systems, 1.III.1.o. Improved Chemical Analysis Technology for Finger-Printing Organic Contaminants; 1.J: Treatment of Fuels in Groundwater, 1.I.1.e. Process to remediate Groundwater

Contaminated with Hydrocarbon Fuels; and 1.T: Bioassay/Biomonitoring Methods; 1.III.1.j. Long-term, In-place Monitoring of Remediation Effectiveness and 2.II.2.e. Improved Biomonitoring Capability.

The specific applied research needs addressed by this project are: (1) the correspondence between apparent oxidation-reduction and hydrogeochemical conditions with major organic metabolite concentration distributions in source, transitional and downgradient zones, (2) the identification of mass distributions (i.e. including solid-associated and aqueous) of the principal electron acceptors, metabolites of regulated compounds and potential organic substrates present in the media (e.g. microbially derived: such as, acetate, formate, etc., and background organics, fatty acids, hydrocarbons and fire-fighting foam constituents), and (3) the temporal and spatial variability in: critical geochemical indicators (e.g. O_2, NO_3^-, NO_2^-, NH_3, Fe_{Total}, Fe^{2+}, Mn_{Total}, Mn_{Diss}, CO_2, CH_2 and CH_4) and major metabolites (e.g. formate, acetate, propionate, as well as, benzoic, toluic, salicylic acids and isomers).

This applied research project builds on the basic work begun with USEPA-NRMRL support (Barcelona, Tomczak, Lu & Virkhaus, Petroleum Hydrocarbons in the Subsurface Conf, In-Press, 1993) which had the general goal of redox-specific characterization of organic matter in both contaminated and uncontaminated aquifers. In this work, major fractions of soluble organic matter and acidic metabolites from the microbial decomposition of hydrocarbon fuels were determined. It showed the importance of hydrogeologic and oxidation-reduction (i.e. redox) potential control over major transformation pathways and that significant degradation of fuel constituents occurs even under anoxic or reducing conditions. The methods developed in this work and that of Cozzarelli et al. (Geochimica Cosmochimic Acta, In-Press, 1993; Environ. Geol. Wat. Sci., 16, 293-297, 1990) are directly applicable to monitoring the progress of microbial processes which occur under a variety of subsurface remediation measures (e.g. air sparging, bioventing, solvent or surfactant flushing). The project's emphasis on both inorganic and organic indicators of bioremediation will aid in the definition of cleanup benchmarks and endpoints. It directly addresses the approach to answering the question of "how clean is clean"?

7. Project Description:

The overall goal of the project is to determine those hydrogeochemical conditions under which hydrocarbon fuels can be degraded in the subsurface with an emphasis on: major transformation conditions and pathways, mass distributions of both source-related compounds and metabolic products, and the spatial and temporal variability in these distributions which bear on the extent of bioremediation efficiency. It directly relates to the Cleanup Thrust Area's R & D objectives which aim at both verifiable and cost-effective site investigation, characterization and remediation technologies.

The objectives of the work include: (1) Hydrogeochemical Zonation; determination of the correspondence between redox and hydrogeochemical zones of the subsurface with loci of microbial transformation, (2) Contaminant Distributions; determination of the fractionation of critical inorganic and organic transformation indicators in water and aquifer solids, and (3) Spatial and Temporal Variability; determinations of the variability in the mass distributions to evaluate

techniques for volumetric averaging and performance criteria for bioremediation operations. The project has been designed to be conducted in parallel with either operational or experimental remediation efforts at sites where hydrocarbon fuels constitute a contamination problem. As such, the project can be conducted at any number of DoD or DOE installations where access can be assured. The Wurtsmith AFB, Oscoda, MI, would be an excellent candidate site given our familiarity with the hydrologic setting, hydrogeochemistry and the focus on bioremediation at the site. It represents a "fast" site characterized by potentially high fluxes of both nutrients and water, as well as high hydraulic conductivity which facilitate high biodegradation rates and potential options for engineered enhancements (Hickman et al. J.W.P.C.F. 61, 9, 1564-1575, 1989).

The three main objectives of the project will be approached in a phased manner building on the existing array of monitoring points and initial site data review. Overall scheduling is flexible based on a FY94 or FY95 start.

Phase 1. Initial Reconnaissance and Delineation of Hydrogeochemical Zones. The existing array of monitoring wells will be sampled and preliminary borings will be made taking water and solid samples at alternate depths for the initial delineation of redox-zones. Field analyses will include: O_2, temperature, pH, conductance, Fe^{2+}, NO_3^-, NH_4^+, alkalinity, CH_4, CO_2, and volatile organic compounds (VOC's). Solid and H_2O samples will be returned to the lab for determination of: total VOC's, inorganic and organic carbon, extractible acid metabolites and intermediates, non-volatile organic compounds (e.g. hydrocarbons, fatty acids, surfactants, fire-fighting foam agent), total Fe and Mn. Appropriate microcosm experiments will be run to evaluate biological activity in selected redox zones. On the basis of these results the initial hydrogeochemical zones and loci of bioactivity will be located and geostatistical estimations of sources and downgradient plume composition will be done. Selected areas for supplemental borings will be determined to expand the biomonitoring array in Phase 2.

Phase 2. Development of Optimized Biomonitoring Network and Long-Term Microcosm Experiments. The geostatistically (kriging) based distributions of redox/hydrogeochemical zones and loci of bioactivity include levels of confidence in estimating concentrations between known points. Supplemental borings and water sampling points will be located to reduce uncertainty within regions of the subsurface and the field and lab work in Phase 1 will be repeated with improved resolution. Refined estimates of background conditions and total contaminant mass per unit volume of aquifer will be developed and the network will be optimized (i.e. minimizing uncertainty) for the evaluation of spatial and temporal variability in critical indicators of contaminant removal. The approximate rates of biotransformation of the principal contaminants from microcosm experiments will be evaluated with respect to increases in metabolic products and correlated with the distributions found in the field.

Phase 3. Evaluation of Variability and Net Bioremediation Over Time. The network will be sampled at intervals (e.g. quarterly) to evaluate temporal and spatial variability in redox/hydrogeochemical zonation and progress of contaminant removal/metabolite production. It is anticipated that the methods we have used in past work (Barcelona et al., Environmental Science and Technology 25, 5, 991-1003, 1989) will serve to control sampling and analytical

error so that actual subsurface variability can be determined at known levels of confidence. Seasonal effects on nutrient supply, dispersion and transport will be evaluated at selected intervals simulating the field results with stepwise applications of two-dimensional flow and transport models. It is likely that at least eight quarters of data collection will be needed to evaluate these effects. Borings will be taken and characterized as before to benchmark the progress of bioremediation and estimate time frames for net contaminant removal.

8. Expected Payoff:

The results of the work will provide a conceptual model for the design and operation of cost-effective remediation efforts. Minimizing the number of wells/borings at such sites and uncertainties in contaminant distributions while providing known levels of confidence in net contaminant removal will reduce the life-cycle costs of remediation efforts. Also, definable benchmarks for evaluating the performance of remediation efforts will serve to better allocate fiscal and human resources at DoD and DOE installations.

In order for benchmarks for the evaluation of the potential success for intrinsic bioremediation to be useful and valid, standard procedures must be developed for contractual use. An additional payoff of this project is the development of analytical procedures that will be reviewed for approval by the EPA to be designated as Standard Methods for contractor use. Personnel on this project are collaborating with Dr. John Wilson and the Air Force in developing protocols for fuel hydrocarbons and chlorinated hydrocarbons. We are actively participating in refining methods for microcosm tests, field quantification of hydrogen gas and quantification of biologically available iron III in core samples. These procedures will become routine characterization methods in standard protocols that are in development as both screening tools and actual implementation of intrinsic bioremediation protocols.

9. Milestones/Accomplishments:

Phase 1

a. Initiate Reconnaissance (borings, water sampling/microcosm setup)	07/95
b. Initiate microcosm setup	07/95
c. Initial well water sampling	08/95
d. Delineation of Hydrogeochemical Zones	12/95
e. Initiate quarterly sampling	12/95
f. Correspondence between loci of bioactivity and hydrogeochemical zones based on results of first six months of sampling	05/96

Phase 2

a. Initiate Quarterly Sampling	10/96
b. Supplemental Borings/Water Sampling/Microcosms	01/97
c. Estimation of Bioremediation Rates	04/97
d. Geostatistical Refinement of Network	02/98

Phase 3

a. Continued Quarterly Sampling	03/99
b. Complete refined estimates of mass removal	03/99
c. Complete conceptual Model Development	03/99

Phase 1 Milestones have largely been completed. Reconnaissance, microcosm setup, well water sampling and delineation of hydrogeochemical zones have been completed. Quarterly sampling is approximately one month off schedule.

A unique method for corroborating redox parameters has been initiated at Wurtsmith AFB by installing nylon rods (VIMs) through the vadose and saturated zones in the identified hydrogeochemical zones for the purpose of examining the occurrence of native mineral deposition. This is a variation of published work in the marine literature used to determine actual redox conditions in sediments.

Significant progress has been made in refining methods for hydrogen gas determinations, iron III determination in soil cores and microcosm protocol development. This work is being conducted in cooperation with Dr. John Wilson and the Air Force in an effort to develop EPA Standard Methods for evaluation of intrinsic bioremediation. The work will have significant impact on agency policy.

10. Transition Plan:

In addition to peer-reviewed papers and reports which will issue from the project it is clear that technology transfer must occur within DoD, DOE and the environmental restoration community. Public presentation at conferences, short-courses, and workshops which we support will be enriched in the future by the results of the project. We would welcome the opportunity to offer focused short-courses for DoD and DOE personnel as well as contractors to broaden the communication of results. It is likely that a pilot course could be offered at the experimental site(s) during the project period if logistics can be arranged. A two-day monitoring short-course with field exercises has been budgeted for Year 2 of the work (FY96). The pilot course could be made part of the project review process involving DoD or DOE project officers, AFIT staff and others as participants.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	550	200	100	850

12. Performers:

Dr. Candida West of the USEPA-RSKERL will be the project manager and provide overall direction of the laboratory work on non-volatile organic compounds and microcosm studies. Dr. West's current research activities include identification of dissolved and solid-associated organic carbon compounds associated with sorption and biodegradative processes. The participation of faculty and graduate students from the host institution of Dr. Michael Barcelona will be key to the project. Dr. Barcelona has worked with both the USEPA-RSKERL and EMSL-Las Vegas laboratories for the past thirteen years, bringing considerable benefit to the field of groundwater contaminant monitoring and subsurface geochemistry during this period.

13. Principal Investigator:

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14. Keywords:

Subsurface Remediation, Bioremediation, Monitoring Network Design, Geostatistics, Cleanup Endpoints, Contaminant Transformation.

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Mobile Underwater Debris Survey System (MUDDS)

3. Agency: Navy

4. Laboratory: Naval Surface Warfare Center, Dahlgren Division

5. Project ID: #52

6. Problem Statement:

The goal of the MUDSS project is to demonstrate the technologies necessary for underwater surveys of shallow water inland and coastal sites littered with ordnance. A successful demonstration will prove the concept of a trailerable, low-maintenance, catamaran-based system capable of finding and mapping the locations of ordnance ranging from small shells to large bombs in water depths of from four to forty feet. MUDSS will supply the object detection and classification technology necessary for the environmental cleanup of ordnance at scores of underwater ordnance litter sites.

To solve the underwater ordnance search and mapping problem it addresses, MUDSS will marry technologies CSS has been developing over the past twenty years for similar minehunting problems with data fusion and visualization technologies developed at Jet Propulsion Laboratory (JPL) for NASA.

7. Project Description:

The technical objective of MUDSS is to demonstrate sensor and processing capabilities which enable (1) the detection and classification at underwater sites of ordnance that may be partially or fully buried in sediment, and (2) the discrimination between ordnance and false targets in the area such as rocks and sea shells.

To accomplish this objective, existing acoustic, magnetic, electro-optic (EO), and chemical sensors and associated signal processing hardware and software developed for other Navy and JPL projects will be leveraged for the MUDSS application. To minimize risk, the project was designed to have two phases:

> The purpose of Phase I (Sep 94-Sep 95) was to assemble a prototype MUDDS and execute a feasibility demonstration (FD) against an ordnance target field in very shallow water (VSW) at CSS.

The purpose of Phase II (Sep 95-Dec 97) was to refine the MUDDS prototype and execute a technology demonstration (TD) at an ordnance litter site.

CSS successfully addressed the similar problem of proud and buried bottom mine minehunting for deeper water (depths greater than thirty feet) in the late 1980's through the development of superconducting magnetic field gradiometer and active synthetic aperture sonar technologies in the MADOM (Magnetic and Acoustic Detection of Mines) developmental program. This program culminated in a successful ATD in 1990. A large follow-on technology development effort (the Mine Reconnaissance/Hunter, or MR/H, program) is now underway at CSS to further improve the Navy's minehunting capability in very shallow water. MUDSS is very similar to MADOM and MR/H, and will leverage $8.6M of the Navy's FY 93-95 investment in MR/H.

The cost of the MUDSS processing development is minimized by using a COTS (commercial off-the-shelf) hardware design for the required 2 Gflop processor similar to a design used for the MR/H processor; by taking advantage of automated classification algorithms for sonars and gradiometers developed at CSS for other programs; and by leveraging $7.0M of JPL's FY 93-95 processor hardware, automatic target recognition, sensor fusion, and 3-D visualization development programs for NASA.

The MUDSS project will have four tasks:

- Sensor suite adaptation and integration
- Automatic target recognition processor (ATRP) development
- Data fusion and visualization tools development
- Platform system development, systems engineering, and MUDSS demonstration

The task objectives and approaches are described below.

Sensor suite adaptation and integration task

The task objectives are to modify sensors that have been or are being developed by other programs and to integrate them into a sensor suite capable of:

- high resolution, multi-aspect acoustic imaging of proud or shallowly buried ordnance in SW/VSW at ranges up to 50 m
- high resolution optical imaging of proud ordnance in SW/VSW at ranges up to seven optical attenuation lengths
- multi-target magnetic localization of buried and proud ordnance at ranges up to 50 m
- short-range chemical detection of explosives

The task approach in Phase I is to:

- Assemble a prototype MUDSS sensor suite of modified and/or refurbished off-the-shelf sensors: the MADOM gradiometer (SGMS), CSS's High Performance Sidescan Sonar,

the MADOM synthetic aperture sonar, the MR/H EO sensor, and the JPL mass spectrometer explosives detector (MSED).
- Collect ordnance test articles for the FD and measure their magnetic moments, acoustic target strengths, EO reflectivities, and underwater chemical signatures.
- Expand the CSS magnetics performance prediction model (MAPPS), the CSS acoustics performance prediction model (SWAT), the CSS electro-optic performance prediction model (IMPERSonator), and JPL mass spectrometer performance prediction model (MSEDM) to include the target and environmental parameters of the FD, and predict the prototype sensor suite performance.
- Validate these expanded models, or improve them as necessary, using the FD data.

The task approach in Phase II is to:

- Use the validated performance prediction models to determine modifications to the proposed MUDSS TD sensor suite. Use SWAT to design changes to the MR/H sonars to optimize SW/VSW performance against the selected ordnance target types; IMPERSonator to determine modifications to the MR/H EO sensor; MAPPS to select between SGMS and a room temperature gradiometer (RTG) being developed by a Navy Special Warfare program; and MSEDM to determine modifications to MSED.
- Modify the MR/H sonar and EO systems as necessary; refurbish the SGMS gradiometer probe, data link, and dewar if RTG is not selected; and modify MSED as necessary.

<u>ATRP (Aided Target Recognition Processor) development task</u>

The task objective is to develop a high-speed (approximately 200 Mbit/sec) computer system for MUDSS sensor suite operation, automatic target detection and classification, and 3-D visualization of fused sensor data in a noisy and cluttered background.

The task approach in Phase I is to:

- Modify and improve existing CSS automated acoustic and magnetic target classification routines.
- Develop initial EO morphological classification routines.
- Exercise the classification routines off line against the FD data.

The task approach in Phase II is to:

- Design and build a COTS-based sensor operation system and processor.
- Develop improved classification routines and implement them on the processor for real-time operation during the TD.

Data fusion and visualization tools development task

The task objective is to develop a near real-time, dynamic, 3-D visualization capability to provide real-time feedback to the survey operation and, following the survey, optimally display the multi-sensor data survey results to the remediation teams.

The task approach in Phase I is to:

- Develop prototype visualization and fusion tools for the MUDSS sensor suite.
- Exercise these tools off line against the FD data.

The task approach in Phase II is to:

- Refine and expand the MUDSS visualization and fusion tools.
- Implement these tools on the ATRP for near real-time operation during the TD.

Platform system development, systems engineering, and MUDSS demonstration task

The task objectives are to:

- Develop a towed vehicle system based on a trailerable, low-draft, low-maintenance, single unit catamaran platform for MUDDS.
- Perform the prototype and technology demonstration system integrations.
- Execute the MUDSS feasibility and advanced technology demonstrations.

The task approach in Phase I is to:

- Design and procure a low-cost, commercially available, non-magnetic catamaran, winch, depressor towed vehicle to deploy the MUDSS prototype sensors and to house the data acquisition system.
- Plan and execute the feasibility demonstration.

The task approach in Phase II is to:

- Refine the Phase I catamaran-based vehicle system for the technology demonstration.
- Perform system integration and execute system configuration control for the technology demonstration system.
- Plan and execute the technology demonstration.

The MUDSS project supports the Clean-Up Pillar of the DoD's Tri-Service Environmental R&D Strategic Plan with specific application to requirement number 1.III.2.f for improved site characterization and monitoring/sensing. No military platform is required.

8. Expected Payoff:

With its capacity to map the locations of ordnance from small shells to large bombs in all coastal or inland waters with depths between four and forty feet, MUDSS will be a capable clutter surveying system for scores of underwater ordnance litter sites. Each MUDSS sensor will outperform any COTS sensor, and the integrated MUDSS system will provide performance against ordnance (including buried ordnance) far exceeding any COTS system. As a self-contained, easily transportable, low maintenance, and low operating cost system whose development costs have been heavily born by parallel Navy and NASA programs, MUDSS will be efficiently amortized.

9. Milestones/Accomplishments:

1. Complete Technology Demonstration System Design	04/96
2. Complete ATRP Algorithm Development	09/96
3. Complete Modifications to Towing Platform	12/96
4. 6.2 Sensors Available for MUDDS	01/97
5. Complete Towed Vehicle Systems for the Sensors	05/97
6. Complete Chemical Analyzer	05/97
7. Demonstrate Real Time ATRP	06/97
8. Demonstrate Data Fusion and Visualization	06/97
9. System Integration and Tests	07/97
10. Technology Demonstration	09/97
11. Data Analysis and Report	12/97

All of the MUDDS Phase I tasks outlined above have been accomplished. The successful execution of the feasibility demonstration, which was the main goal of Phase I, was completed September 21, 1995 and represents a major accomplishment and unqualified success. Large quantities of high quality data have been obtained against an OEW target field with all sensors operating both singly and in various combinations (41 runs of a total of 140 were taken with all sensors operating simultaneously). This data was exercised with the ATRP algorithms and visualization tools developed in Phase I and demonstrates the viability and power of sensor fusion for underwater OEW surveying.

10. Transition Plan:

A viable transition to a commercial capability is ensured by the early insertion of industry into the MUDSS program. CRADA's and/or procurement will be used to provide industry sensor, sensor fusion, data processing, visualization, and system integration expertise.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	1,595	575	730	1,120	180	4,200

12. Performers:

CSS and JPL are the lead performers. The magnetic sensors for MUDSS are being supplied by Loral Federal System, International Business Machines, Quantum Magnetic and Ball Aerospace; the sonars will be supplied by Westinghouse; Raytheon will supply the EO sensor. CRADAs with Loral Defense Systems and Federal Systems have been established for technical exchange on laser systems and systems engineering.

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14. Keywords:

Gradiometry, Acoustics, Electro-Optics, Mass Spectrometry, Fusion

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Application of a Neural Network Model (NNM) Coupled with Genetic Algorithms to Optimize Soil Cleanup of Subsurface Contamination

3. Agency: U.S. Army

4. Laboratory: Cold Regions Research Engineering Laboratory (CRREL)

5. Project ID: #1049

6. Problem Statement:

Cleanup of contaminated soils is of paramount importance for the safe and continued operation of numerous military installations. Soil conditions in cold climates add another level of complexity to the subsurface cleanup problem. Furthermore, understanding groundwater flow and contaminant transport in soils that experience seasonal frost penetration, rapid runoff/snowmelt conditions, or zones of discontinuous permafrost requires special cold-regions modeling techniques. Additionally, the prohibitive expenses associated with a site remediation dictate the implementation of an optimized cleanup strategy. Consequently, there is a need to develop capabilities like this proposed Neural Network Model (NNM) coupled with genetic algorithms to enhance analysis and optimization of subsurface conditions and treatments for soil cleanup.

This SERDP effort has two targets under the cleanup area for contaminant fate, transport, and remediation of soils, especially cold climate soil conditions. The first objective is the automatic decomposition of Ground Penetrating Radar (GPR) signals into stratigraphic layers using NNM. The GPR can probe the subsurface non-invasively at high resolutions. However, quantitative interpretation of these data are sparse. We propose to train Neural Networks, which are ideally suited for pattern recognition, to recognize various stratigraphic layer configurations. With this tool in place, enhanced site conceptualizations become available.

The second objective is the optimization of remedial treatment strategies using NNM coupled to Genetic Optimization Algorithms. In the NNM, the Neural Network would be trained to recognize a contaminant distribution as a function of the boundary conditions. The Genetic Optimization Algorithm would assist the decision analysis of various remediation strategies based on the simulated behavior predicted by the NNM.

The coupling of these applied research areas (Neural Network techniques, Genetic Optimization, and GPR) yields a technology demonstration that holds the promise of illuminating the subsurface stratigraphy and the deployment of an optimum remediation strategy.

7. Project Description:

Prior to any realistic contaminant predictions, an accurate site conceptualization is required. This task has been difficult and expensive to develop. The size-of-scale constraints have simply exceeded available financial and manpower resources. Variability of subsurface stratigraphy separated by one or two meters can affect the groundwater flow in an entire region significantly. However, core sampling occurs on length scales measured in 100 - 1000 meters. Ground Penetrating Radar (GPR) signals can probe the subsurface non-invasively at resolutions far smaller than that required for groundwater modeling. Extensive GPR data has been collected on several sites at Fort Wainwright, AK and elsewhere. Unfortunately, a systematic, repeatable decomposition of these signals into stratigraphic layers such as top-of-permafrost, bottom-of-permafrost, water table, and top-of-bedrock is lacking. Several Neural Network strategies, expert system approaches, and Chirp-Z transform techniques have been successfully developed and/or employed by the authors for the detection of layered interfaces in metals and composites, similar to the soil layer strata in the ground. These previous Ultrasonic Nondestructive Evaluation (UNDE) simulations incorporated the physics of a linear elastic system. A similar operation will be required for the GPR situation. A key and unique feature of this model effort will be the use of Neural Network techniques on concert with the traditional governing equations for elastic wave propagation.

For the NNM development, the governing equations describing the physics of a linearized soil system subjected to GPR signals will be formulated. Several realistic configurations of the subsurface will be simulated which, for the special case of cold regions, includes discontinuous zones of permafrost and varying water table elevations. These simulations will serve as a training set of signals to teach the Neural Network pattern behaviors from known, idealized subsurface stratigraphies. Based on the learning progress, the Neural Network Architecture and/or training sets will be adjusted.

A. NNM Training and Validation

As a second stage in the project, actual GPR data will be used to train and validate the NNM. The GPR data collected at Fort Wainwright are ideal since numerous ground-truthing cores have been examined for correlation with the GPR data. With this NNM trained and validated, a series of GPR signal can be fed into the system and the subsurface stratigraphy quantified in real time. This modeling strategy can be used for non-invasive evaluation of the subsurface in general, in all climatic regions. However, the soils and moisture content of Fort Wainwright are ideal for the initial stage if the program. Fort Wainwright soil is comprised of glacially derived sands and gravels (Chena Alluvium) that were transported and repeatedly reworked by the Tanana River, and to a lesser extent by the Chena River. The alluvium is reported to be very transmissive with no well-defined stratigraphy. Additionally, the groundwater elevation in this region is within 10-20 feet of ground surface. The well mixed soil coupled with the high water table provides a good GPR signal. This body of existing field data from Fort Wainwright provides ample data information to effectively calibrate and validate the proposed Neural Network Model.

B. General Application of NNM

Pattern recognition using NNM has broad application beyond detection of permafrost and/or bedrock. Hence, NNM is applicable to the soils encountered in different contaminated military sites other than those in cold regions. After the subsurface stratigraphy is developed with the help of our Neural Network recognition system, genetic algorithms for the optimization of remedial treatments will be applied. CRREL's research efforts in groundwater flow and contaminant fate and transport are leading the hydrogeology community in cold-regions applications. However, after a site conceptualization has been established and the contaminant fate and transport forecast, what is the best remedial treatment? It is proposed that a Neural Network Model coupled with a genetic optimization algorithm be employed to assist in the decision analysis of various remediation strategies and of various deployments within a remediation treatment for various cleanup sites.

A key feature of the genetic optimization system is that it avoids the pitfalls of most optimization algorithms which follow a gradient approach. These latter strategies are plagued with local minima search terminations. The genetic algorithms have a mutation function that allow the system to examine alternate settings and not be bounded by local minima.

We propose to develop these algorithms for the deployment of monitoring stations at remedial sites. The genetic optimization strategy should produce the best deployment pattern and scheduling of monitoring sites. This optimized layout will ensure the successful monitoring of the contaminant fate and transport without incurring unnecessary expenses.

8. Expected Payoff:

The expected benefits of this project are an accurate non-invasive site conceptualization and an optimized monitoring deployment plan for remediation. The ability to characterize the site will increase by two orders of magnitude from current practices. The gains realized in predicting contaminant flow would be an order of magnitude. The optimized deployment routines could reduce the monitoring cost of a contaminated site by one-third.

The potential opportunity to transfer this technology to conventional sites (not cold-regions, but good moisture content) is excellent.

9. Milestones:

1. Numerically formulate wave propagation in permafrost rich soils	06/96
2. Acquire, map, and catalog existing GPR data	08/96
3. Interim report - comparison of numerical wave propagation to GPR field data	09/96
4. Formulate Neural Network Model Architecture and training methodology	11/96
5. Test/train NNM with idealized training set (stage 1)	01/97
6. Validate NNM using GPR data correlated with ground-truthing cores	03/97
7. Formulate genetic optimization algorithms for remediation strategies	04/97
8. Train NNM to predict groundwater flow based on boundary conditions	06/97
9. Interim report on stratigraphy predictions using a Neural Network	09/97

10.	Train NNM to predict contaminant fate and transport based on sorption, decay, dispersion, and boundary condition parameters	10/97
11.	Couple the NNM and Genetic Optimization routines to predict remediation	06/98
12.	Final report	09/98

10. Transition Plan:

The project results (interim and final) will be presented at symposia and workshops associated with hazardous waste treatment and cleanup. General conference on site remediation sponsored by EPA, API and others will document our efforts. Interim reports will be enhanced for submission to refereed journals on remediation, contaminant transport, advances in water resources, and computional methods in water resources. CRREL staff and cooperators will develop presentations to be given to interested DoD organizations.

11. Funding: $(K)

FY96	FY97	FY98
196	250	195

12. Performers:

The performers in this project will include CRREL staff at Fort Wainwright, AK for the evaluation of ground-truthing borehole cores and monitoring of groundwater elevations. Staff at the US Army Alaska Department of Public Works and the Corps of Engineers Alaska District, with whom we have worked closely in previous project on subsurface analysis at Fort Wainwright, will assist with field data acquisition and interpretation. Dr. Lawson performed the GPR studies and will interface with this group for transfer of GPR data and interpretations. Mr. Currier will be the project manager. Professor Ludwig will work jointly with Professor Sullivan on the decomposition of the GPR data.

13. Principal Investigator:

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14. Keywords:

Neural Network, Genetic Optimization, Ground Penetrating Radar, Stratigraphy, Contaminant Transport Modeling, Non-Destructive Evaluation

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Natural Attenuation of Explosives Contaminants

At time of printing, a detailed project description had not been received.

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Rapid Detection of Explosives and Other Pollutants

3. Agency: U.S. Navy

4. Laboratory: U.S. Naval Research Laboratory

5. Project ID: #28

6. Problem Statement:

This 6.26.3 project addresses Requirement 1.III.1.i. "Improved sensor technologies for measurement of environmental pollutants". The DoD has over 1200 sites contaminated with explosives and 87% of these exhibit contamination in the groundwater. Remediation of munition sites contaminated with explosives and monitoring of the surrounding area requires accurate analyses of field samples. Tests should be conducted rapidly and on site for the most effective remediation to proceed. NRL has previously developed a biosensor which can be configured to measure either discrete samples containing explosives in under one minute or to monitor process streams at timed intervals. Using a displacement immunoassay, multiple samples can be injected into a microcolumn containing a fluorescent explosive molecule bound to immobilized antibody. If explosives are present in a sample, the fluorescent molecule is displaced and detected. If the sample contains no explosive molecules, reagents are not expended.

The objective of the present work is to use the existing biosensor developed at NRL for explosives detection to test soil and water samples from known sites of contamination. Operating parameters for selected molecules, including detection limits, possible interferents in samples, and useful system lifetime will be investigated. If the laboratory studies are successful, we will perform on site analyses for explosives.

7. Project Description:

Assays for a number of relevant explosives, including TNT, RDX, PETN, and DNT have been developed for the Flow Immunosensor. To adapt this technology for site characterization, the primary tasks in the first year of funding were to look at field samples on the laboratory device and minimize problems due to background noise from interferents. Since environmental samples often contain multiple species which could interfere with fluorescence detection, particularly at emission wavelengths less than 550 nm, it was necessary to examine field samples for intrinsic fluorescence and select a signal molecule that fluoresces outside the range of background noise. A new fluorescent dye that became available recently greatly reduced these problems. The dye, Cy5, is excited in the red region (630-650 nm excitation), where there is little natural fluorescence from the environment. These dyes, as well as others that emit in the upper

wavelengths, were linked to the explosives and tested as signal molecules in the Flow Immunosensor. Samples of explosives were spiked into buffer and into simulated field samples to confirm the sensitivity of the assay. These studied demonstrated that the sensor performed well with environmental samples and exhibited neglible matrix effects.

During this past summer, the Flow Immunosensor was tested in initial field trials at two military bases identified by the EPA as priority Superfund cleanup sites. Conducted at explosives washout lagoon areas on Umatilla Army Depot (Hermiston, OR) and Site F and A at Naval SUBASE Bangor (Bangor, WA), the field study objective was to measure the effectiveness and efficiency of the Flow Immunosensor in performing on-site field analysis for two selected explosives, TNT and RDX. Samples containing unknown concentrations of explosives were collected from groundwater and leachate monitoring wells at various locations, with subsequent analysis in the prototype sensor. In conjunction with the tests performed on-site by the Flow Immunosensor, independent laboratory analysis of identical samples and the explosives standards were performed by High Performance Liquid Chromatography (HPLC- EPA Method 8330) for data validation. Field samples were also examined to determine detection limits, possible interferents in samples, and lifetime of biosensor components. Field test results demonstrated the accuracy and precision of the NRL biosensor for detecting TNT and RDX at low part per billion (ppb) levels. In a final comparison of HPLC and Flow Immunosensor data, contour plots drawn using field test measurements showed that site characterization profiles for the NRL method were nearly identical to the HPLC plots. A technical report summarizing these results has been completed.

Based on successful proof-of-principle tests for environmental monitoring with the Flow Immunosensor, work has proceeded on engineering a portable device. A contract to engineer a field portable device was awarded to Research International in late FY95 (August), with an expected delivery date for a prototype instrument of late March 1996.

Future efforts will focus on developing soil testing methods for the sensor. In addition, we will be continuing our collaboration with the EPA to validate the instrument in the field at selected sites. If funds become available, we will begin a EPA demonstration project.

8. Expected Payoff:

The flow immunosensor has many advantages over existing technologies.
The major advantages of the flow immunosensor are in the areas of cost and time. Current procedures for analyzing field samples, such as HPLC or GC/MS, are expensive and time-consuming. Two-three weeks are required to obtain test results, with a single analysis costing between $200-500. Skilled laboratory technicians are needed to perform the analysis. In contrast, single sample tests with the flow immunosensor are expected to cost several dollars. Operation of the sensor is straightforward and fast, and does not require a skilled operator or extensive training. In its simplest version, the user introduces the sample at the beginning of the system and records the results within 1 minute of sample introduction. The widely used methods often require addition of different reagents throughout the assay and lengthy incubation times, or demand the use of large, sophisticated instruments. Even if an initial sample extraction procedure

is required, the solvents required are less noxious than the solvents used to prepare samples for GC or HPLC analysis. In the NRL sensor, all the components required to recognize the target in an aqueous solution and release a signal are contained within a small column.

The flow immunosensor is also well-characterized. Experimental parameters, including column size, antibody density, and flow rate, have been studied extensively. Using a mathematical framework recently developed, we are able to predict the behavior of the sensor for a given antibody-analyte pair. In addition, because the immunosensor is antibody-based, detection is extremely specific for the target molecule.

System manufacturing costs and portability are also important considerations. The components of the current system are inexpensive and off-the-shelf. Cost for the laboratory prototype is under $10,000, and the sensor can be engineered to fit into a single briefcase with microprocessor control.

An additional strength of the NRL flow immunosensor is its adaptability for use in a variety of environments. It can be readily used with individual samples injected by hand, air samplers that extract vapors into water, or super sipper systems that rapidly inject samples from hundreds of vials. In addition, the device can be used either for continuous monitoring of a water stream, or for testing discrete samples in under a minute, allowing on site analysis for site characterization or remediation.

Finally, the detection limit of the flow immunosensor is already comparable to established, more complicated systems. Using the NRL sensor, cocaine and TNT in water have been detected at levels of less than 5 parts per billion (equivalent to 5 ng/ml). This level of sensitivity is well-below that obtained using precipitation, dip stick, most enzyme immunoassays, and fluorescence polarization methods, and is comparable to radioimmunoassays.

The flow immunosensor has already been shown to have extreme specificity, sensitivity, and the versatility required to detect a wide range of molecules. This technology is expected to be particularly relevant for testing groundwater, streams and lakes for wastes from explosive manufacture, for monitoring chemical and fuel storage, and for checking the progress of bioremediation efforts. If married to air samplers and aqueous extracts of soil samples, the device can also be used for monitoring ground contamination.

9. Milestones/Accomplishments:

1. Prepare technical summary of field trials.	11/95
2. Collaborate with Research International on portable device fabrication.	02/96
3. Conduct tests on environmental samples in the lab and in the field.	04/96
4. Field test portable sensor at selected cleanup sites.	09/96
5. Field trial report	11/96

The primary task is to adapt the current TNT sensor for use in environmental testing. In the six weeks since project startup, we have synthesized a fluorophore-labeled TNT which can be excited

by small diode lasers in the near IR-range (650-670 nm). The conjugate, Cy5 cadaverine-TNT, was tested and found to bind specifically to the anti-TNT monoclonal antibody. In addition, to simplify reagent preparation for the sensor, a new type of polymer bead, developed by 3M, with better flow properties and improved protein immobilization was prepared. Experiments using these reagents in the laboratory prototype sensor demonstrated quantitative detection of TNT in buffer samples at the low ng/ml level.

10. Transition Plan:

The EPA has indicated an interest in setting up a one-year demonstration of the Flow Immunosensor at its remediation site in Bangor, WA. The small, fieldable instrument that can be used to characterize contaminated sites would be provided to the end user.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	112	125	200	200	637

12. Performers:

The primary performers for this project will be personnel from NRL's Center for Bio/Molecular Science and Engineering. The portable device is being fabricated under a contract with Research International, Woodenville, WA.

13. Principal Investigator:

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14. Keywords:

Biosensor immunoassay, environmental monitoring, antibody/antigen, explosives detection

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Trichloroethylene Risk Assessment

3. **Agency:** U.S. Air Force

4. **Laboratory:** Armstrong Laboratory

5. **Project ID:** #115

6. **Problem Statement:**

Chemical contamination of groundwater and soil is a national problem which consumes extensive technological and financial resources. Cleanup levels are determined on the basis of risk calculations, usually requiring extrapolation from laboratory animal studies. Determining acceptable levels for humans from animal studies is a conservative, policy driven process that involves extrapolation and interpretation of scientific findings. Scientific uncertainties in this process are often compensated for by conservative assumptions that result in lower cleanup levels with inherent increased costs.

Current costs to clean up to the low ppb range in water and soil are in the hundred of millions of dollars. Operating costs of a groundwater treatment system for a single plume at Wright-Patterson AFB, contaminated with high levels of trichloroethylene (TCE), are $1.3 million/year. TCE remediation at 31 DoD installations has cost $670 million to date, while work for all solvents has cost $2 billion. It has been estimated that for 125 Air Force sites with TCE contamination, raising the drinking water standard from 5 to 50 ppb would save $620 million.

TCE, tetrachloroethylene, and other volatile organics are priority groundwater contaminants for DoD and the US EPA. These chemicals often greatly exceed current risk-based cleanup levels at Superfund landfill sites. This project is designed to further the development of newer risk assessment methodologies for developing reasonable health protective criteria for important groundwater contaminants for use in establishing cleanup requirements.

7. **Project Description:**

The goal of this project is to develop innovative risk assessment methods that are applicable to common volatile organic water and air contaminants for use in development of scientifically defensible cleanup criteria. Objectives have been defined in each of the areas of the four step risk assessment process: hazard identification, exposure assessment, dose-response assessment, and risk characterization. The objectives focus particularly on the critical dose-response assessment step in light of the efforts by US EPA to adopt revised guidelines for Cancer Risk

Assessment. TCE will be used as the case study chemical for development of these approaches concluding with development of Provisional Remediation Goals.

This project is a joint venture for Air Force, Army, Navy, and US EPA that has had national and international input and cooperation from academic and industrial sectors. Many elements of this program were reviewed and supported at an international TCE Workshop which included nearly 40 leading researchers and policy analysts from academia, industry, US EPA, and DoD in areas of epidemiology, metabolism, pharmacokinetics modeling, tumor promotion, peroxisomal proliferation, biological effects modeling, and risk assessment.

This project is an enhancement of a previously funded SERDP applied (6.2) project. It contributes directly to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: 1.V Risk/Hazard Assessment and 1.X: Hazard Assessment. Methods developed in this project are generally applicable to the development of risk based criteria.

Objective 1: Evaluate new EXPOSURE ASSESSMENT approaches to address the future use scenarios used to derive cleanup criteria.

1.1 Evaluate utilization of probability (Monte Carlo) analysis for future use exposure scenarios for volatile organics in water such as drinking (oral) or showering (inhalation).

Objective 2: Improve DOSE estimation across species (mouse, rat, human) using physiologically based pharmacokinetics modeling and supporting research.

2.1 Expand PBPK modeling beyond its current strength with volatile organics, to better address toxicologically relevant water soluble compounds such as metabolites of TCE.

2.2 Improve quantitative descriptions of the metabolic pathways and uptake mechanisms for TCE and its metabolites in mice, rats, and humans using appropriate *in vivo* and *in vitro* laboratory studies.

2.3 Evaluate the pharmacokinetics competency of carcinogenic metabolites of TCE to account for the cancer induced by the parent compound.

Objective 3: Improve RESPONSE comparisons across species using alternative modeling approaches and supporting research.

3.1 Evaluate the correlation of biomarkers of the cancer process with production of radicals during TCE metabolism.

3.2 Develop conceptual frameworks for biological based dose-response (BBDR) modeling to integrate pharmacokinetics (exposure, dose, tissue-dose) with markers of early and late biological responses.

Objective 4: Propose new RISK CHARACTERIZATION strategies for utilization in development of cleanup criteria.

4.1 Evaluate the implications of alternate dose-response modeling methods for acceptable risk levels.

4.2 Recommend Provisional Remediation Goals for TCE to DoD and draft suggestions to US EPA for TCE risk assessment under new EPA guidelines.

8. Expected Payoff:

One result of this effort will be to persuade the US EPA to revisit the cancer potency calculations for TCE under the new proposed guidelines for cancer. Dioxin has recently gone through this process. Central to the dioxin issue is the use of a biologically-based response model. Our goal is to have TCE be the second chemical that goes through the new cancer guideline evaluation process. The result could be savings of millions of dollars in cleanup costs.

Two critical elements are required in working with US EPA. One is to build up the supporting peer reviewed scientific literature to support their decision making. The other is to provide alternatives to the default methodologies that they normally employ. These methods generally incorporate greater scientific information to minimize the use of conservative default assumptions.

This project is designed to provide both of these elements. Alternative risk assessment methods will have great applicability to other volatile organic chemicals whether for developing cleanup criteria, evaluating pollution prevention alternatives, or establishing operating limits on environmental emissions.

9. Milestones/Accomplishments:

1. Interagency agreement with EPA	10/93
2. Literature reviews of TCE and biological determinants of cancer	10/93
3. Initiate *in vitro* metabolism studies	11/93
4. Prepare animal use protocols and research proposal	02/94
5. Complete TCE/vinyl chloride mixture metabolism study	02/94
6. Sponsor TCE Science Workshop	12/93
7. Initiate biologically based modeling	04/94
8. Complete literature reviews for pharmacokinetics of TCE metabolites	06/94
9. Complete development of analytical methods for TCE & metabolites	08/94
10. EPA issue request for proposals, with research agreements to follow	08/94
11. Complete *in vitro* metabolism studies of dichloroacetate	09/94
12. Complete field exposure assessment for TCE	09/94
13. Initiate research on chloral hydrate metabolism	10/94
14. Initiate development of biologically based modeling	03/95
15. Complete studies on early biological effects related to cancer	06/95

16. TCE project coordination meeting	06/95
17. Evaluation of Benchmark Dose approach to lose dose extrapolation	05/95
18. Development of mouse PBPK model, including TCE metabolites	06/95
19. Report on chloral hydrate split in TCE metabolic pathway	08/95
20. Report on probability analysis of drinking water exposure	09/95
21. Initiate Medical College of OH collaboration	11/95
22. Complete human volunteer TCE exposure	12/95
23. Complete rodent and human sample analyses	01/96
24. Initiate model verification & model linking TCE & metabolites	01/96
25. Initiate repeated dosing study	02/96
26. Initiate inhalation study	03/96
27. Complete modeling of human exposure	04/96
28. Initiate inhalation modeling	06/96
29. Initiate dose route effect comparison	09/96
30. Comments to EPA on TCE cancer risk assessment (complete) 12/97	

FY92: Installation of GC/LC-MS for required analytical sensitivity, install/validate human liver slice system, complete TCE/VC mixture studies. FY93: Initiated joint effort with USEPA, completed review of TCE literature/research proposal, conducted TCE workshop for national/international leaders in TCE research. FY94: Completed first human volunteer exposure with extensive TCE & metabolite measurement in urine/blood, completed *in vitro* studies of TCE metabolism in mouse, rat and human, identified specifics of glucuronidation pathway in liver and kidney, SERDP-funded TCE research identified by Dr. Farland (Director, USEPA National Center for Environmental Assessment) as major contributor to global TCE research effort, reevaluation of TCE risk assessment given "Flagship" status (i.e., fast track) by USEPA.

10. Transition Plan:

The Air Force has been appointed the DoD lead agency for TCE issues. This has led to the formation of the Tri-Service TCE working Group. This forum will be used to formally present project conclusions regarding TCE risk assessment to USEPA. Additionally, Dr. Fisher (Armstrong Lab) has been chosen to author one of the EPA TCE risk assessment chapters and project personnel will participate in the peer review of the draft EPA risk assessment.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	1,700	1,400	0	900	900	4,900
EPA	700	700	700	500	500	3,100
Tri-Service Tox			420	330	300	1,050
USAF	200	300	30	200	150	880
ARMY	200	200	200	200		800
NAVY	150	120				270
Total	2,950	2,720	1,350	2,130	1,850	11,000

12. Performers:

This research is being conducted by Tri-Service Toxicology and USEPA, Medical College of Ohio, University of Wisconsin, Wayne State University, University of Wurzburg and the NY State Department of Health are involved in related research activities.

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14. Keywords:

Risk Assessment, Trichloroethylene, Cleanup, Cancer, Dosimetry, Modeling

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Biosorption Treatment of Plasticizers and Solvents

3. **Agency:** US Army

4. **Laboratory:** USAE Waterways Experiment Station (WES)

5. **Project ID:** #711

6. **Problem Statement:**

The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with low levels of plasticizers (acetone) and chlorinated solvents (trichloroethylene [TCE]). Current or traditional treatment technologies available for use in TCE treatment are granular activated carbon (GAC) and air stripping; however, neither technology results in the direct destruction of the organic contaminant. An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the near future for chlorinated solvent oxidation. Remediation costs for all of these technologies generally falls within the $1.00 to $5.00 per 1,000 gallons range. In the case of GAC, treatment of groundwaters containing low levels of chlorinated solvents is not economically feasible.

Acetone poses a very unique challenge to both traditional and innovative technologies. Acetone does not adsorb onto GAC due to its high water solubility, it does not strip in air strippers due to its low Henry's Law constant, and it does not oxidize in chemical oxidation systems due to its stable chemical structure. Acetone is degraded biologically, but biotreatment is unsuitable for treatment of low level contaminated groundwaters because an active biomass cannot be sustained due to low substrate loadings. Unfortunately, most groundwaters contain acetone at relatively low levels; therefore, expensive cometabolite addition is almost always required.

TCE can also be treated using biological degradation. TCE is somewhat more difficult to biodegrade then acetone, but recent advances in cometabolic pathways (methanotrophic) indicate that biotreatment of TCE is feasible. One problem associated with TCE degradation is the tapering off of microbial activity, over time, in continuous and semi-continuous biological systems. Biosorption is almost always associated with GAC. Primarily, GAC is used as a means of extending the service life of a GAC bed by regeneration of the spent carbon within the bed. Recent work on phenolic compounds has resulted in the development of an innovative technology known as biofilters. This technology utilizes GAC as a means of structurally supporting an active biomass.

Organophilic clays (OPCs), have been successfully used to remove low levels of wood preserving waste from contaminated groundwater. Results of this evaluation are encouraging, but disposal

of the spent OPC is a problem. OPCs are innovative adsorbents that have received limited evaluation and application for the removal of TCE.

The USAE Waterways Experiment Station (WES) has conceptualized a treatment system for low level contaminated groundwaters based on biosorption and bioslurry systems. In this treatment scheme, the contaminants are adsorbed onto the OPC until all adsorption sites of the OPC are spent. The spent OPCs are removed from the reactors and then an on-site reactor is used to biologically degrade the adsorbed contaminants. This converts OPC adsorption from a simple phase-change technology into an on-site destruction technology.

This proposed treatment approach is an applied research and technology field pilot application (6.2). This research is an enhancement to an existing FY 93 SERDP proposal.

Specific identified user requirements to be addressed through performance of this work unit include:

Technology for removal of energetics/other organics contamination.
Treatment system for water contaminated with organic contaminants.
Treatment system for water contaminated with chlorinated and defense hydrocarbons.
Treatment of Navy revellent contaminants in salt/brackish/groundwater matrices.
Isolation and treatment technology for contaminated surface water impoundments.
Treatment system for water contaminated with mixtures of chlorinated solvents.
Contamination under buildings and roads.
Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
Improved marine sediment remediation technologies for metals, organics, and PCBs.
Enzyme and bacterial treatment technology.

7. Project Description:

The USAE Waterways Experiment Station (WES) under the Environmental Quality and Technology Program (EQT) is developing a means of biologically regenerating spent GAC. WES also plans to evaluate the use of OPCs for treatment of explosives contaminated groundwater. It is believed that OPC biosorption can be utilized for the treatment of low level explosive contaminated groundwater.

The USAF Tyndall AFB has been active in development of microbial consortia capable of effectively degrading TCE from contaminated groundwaters. This technology can be tailored to interact with the conceptualized OPC biosorption schemes. Tyndall AFB is currently developing a bioreactor for treatment of contaminated groundwater with higher levels of TCE. The consortia developed in these efforts will be useful in the development of the OPC biosorption concept. Tyndall has also developed a surfactant which may further enhance the sorptive capacity of the OPCs. An increase in sorptive capacity will result in improved costs benefits. There has been little or no direct development of OPC biosorption. Past efforts on bioregeneration of spent GAC

containing phenolic compounds indicates promise for the use of microorganisms to degrade adsorbed compounds.

A recent evaluation of OPCs for wood preserving waste treatment indicates the utility of OPCs for groundwater remediation. Unfortunately, there are few options for disposal of spent OPCs (and GAC). Under US Environmental Protection Agency funding, WES has demonstrated the feasibility of using bioslurry systems for treatment of soils contaminated with plasticizers and wood preserving wastes. The contaminated soils used in these studies did contain significant clay fractions.

The overall objective of this study is to develop an OPC based biosorption process. Development of this technology will provide environmental engineers with a practical means of treating acetone. With respect to TCE, this technology may eliminate the problem of TCE activity loss over time.

The development of OCP biosorption into a fieldable technology for site remediation will be approached through a series of tasks detailed below:

a. Task I. The adsorption capacity of various OPCs and other sorbents will be preliminarily evaluated by contacting the sorbent with spiked solutions containing TCE. Three to four sorbents will be selected for further testing in adsorption isotherms. Activated carbon performance will be compared to the performance of the sorbents. One or two of the most effective sorbents will be selected for small column studies.

b. Task II. Evaluation of microbial activity toward adsorbed TCE. Toxicity effects of TCE concentrations on microbial consortia will be evaluated using a respirometer study. The ability of a microbial consortia to desorb and subsequently biodegrade the adsorbed acetone and TCE from the OPC will be evaluated using laboratory batch systems.

c. Task III. Bench Scale Bioslurry Studies. Bench scale studies will be performed to determine process feasibility, verify reaction kinetics and pathways, and set pilot studies test matrices.

d. Task IV. Pilot Scale Studies. Pilot scale studies will be performed using pilot OPC absorbers. The complete pilot system will be designed for complete mobility to other candidate sites. If required, a process gas management system may be used if off-gassing of TCE and the selected cometabolite is deemed problematic. These pilot scale studies will be performed in the field at CRREL. Once completed, the pilot system will be available for field pilot application at other installations.

e. Task V. Draft Report. A report detailing the following will be drafted:

1. Describe techniques on how to perform bench scale treatability studies used for process evaluation during Feasibility Studies (FS).
2. Discuss process feasibility and potential limitations.
3. Present the results from the bench and field pilot studies.

4. Summarize available full scale equipment availability.

The report will be design and applications orientated. The report will serve as a handbook for implementation of OPC biosorption at other field sites.

The information obtained from the performance of this study will assist in meeting several DoD/DOE environmental remediation objectives. This work effort will result in the development of a contaminant-destruction technology applicable toward chlorinated solvent compounds.

Technical issues to overcome as identified to date are to determine if OPCs have appreciable adsorption capacities for TCE; if OPCs can be treated to levels that render them environmentally safe and regulatory acceptable; and if process gas recirculation will be required for TCE biodegradation of the ground OPCs. This project falls under the 1.H and 1.I requirement thrust areas under the Tri-Service Environmental R&D Strategy Plan.

8. Expected Payoffs:

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. OPC biosorption may eliminate problems associated with reduce TCE bioactivity over time. The actual economic benefit is difficult to ascertain due to the innovative nature of the concept. A conservative estimate is that the technology could be implemented at a cost range of $1.00 - $3.00 per 1,000 gallons treated.

9. Milestones/Accomplishments:

Major milestones under this work effort are listed below along with the respective fiscal year they will be completed.

1. Initiate the evaluation of adsorbents	03/94
2. Initiate microbial processes investigations	06/94
3. Initiate bench bioslurry systems	09/94
4. Complete bench scale evaluations	10/95
5. Design and construct pilot systems	12/95
6. Initiate pilot studies	04/96
7. Final report	09/96

Desorption studies evaluating sonification, pH adjustment, and reverse equilibration (reequilibration using "clean" water) are being conducted for acetone and TCE. The microbial strains G4 and PR1 have been obtained and evaluated for their ability to degrade TCE. The propriety strain (PR1) has been identified as a candidate strain capable of degrading TCE. Two TCE degrading strains, PC5 and BF1, were obtained from Envirogen, Inc. The development of an analytical system in conjunction with a biotreatment microcosm has been completed. C-TCE studies have been initiated and TCE mass balance studies have been completed. The monoclonal

antibody against G4 was obtained. TCE degradation studies on PC5 and G4 have been completed. Bench scale column design has been completed and evaluation is to begin.

10. Transition Plan:

This technology development will generally follow the typical transitional path detailed under DoD's EQT Program. Within three years, the technology will be transitioned from a bench concept to an implementable technology. Technical assistance will be available to technology users during design and implementation of OPC biosorption. Collaboration with private organizations for improving process development through CRADAs will be proposed. The technology will be transitioned to the user community through technical papers, presentations, briefings by the performers of this proposal.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	500	750	243	600	2,093
WES	250	250	200		700
USAF	500	500	300		1,300

12. Performers:

The performers for this work unit are USAE Waterways Experiment Station and Tyndall AFB. Advice from OPC manufacturers will be incorporated into the final technical approach for this study.

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14. Keywords:

Biosorption, Bioslurry, Biotreatment, Adsorption, Trichloroethylene, Acetone

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Enhancing Bioremediation Processes in Cold Regions

3. Agency: U.S. Army

4. Laboratory: Cold Regions Research and Engineering Laboratory (CRREL)

5. Project ID: #712

6. Problem Statement:

This project is basic, 6.1 research and has received FY94 SERDP funds. This proposal is for continued funding of the FY93 funded research and expands the scope to include rhizosphere effects. The objectives are to improve remediation ability in areas subject to low temperatures and to facilitate treating large volumes of soil at contaminated sites where low temperatures are inhibitory. Many of these sites are also subjected to extended freezing or freeze-thaw cycling, have short operating seasons, frequently have insufficient soil nutrient levels, and are often in remote locations where cost-effective alternatives do not exist. Easily implemented on-site and in-situ technologies such as biotreatment are needed for soil cleanup at these sites.

The primary strategy in bioremediation is to remove the limitations to microbial activity, but the extensive amounts of soil that are typically involved require using large-volume techniques that necessarily expose soil to seasonal temperature cycles. The net influence of freezing temperatures on the overall rate and extent of soil biotreatment is a complex interaction of microbial and chemical rates, substrate-nutrient solubility and availability, and physical-chemical phenomena. It is not sufficiently understood to exploit or manage biotreatment systems in advantageous ways.

Enhanced microbial activity in rhizosphere zones is documented for some pesticides and may offer a significant mechanism for low-cost soil treatment. Coupled with low-temperature effects, we propose to quantify low-temperature soil-rhizosphere activity and identify relationships with associated plant species. Because bioremediation is often constrained by nitrogen, phosphorus, and carbon co-substrate limitations, we hypothesize that nutrient and co-substrate limitations to bioremediation at remote sites can be overcome by stimulating soil-rhizosphere effects.

7. Project Description:

This effort applies to DoD Pillar 1)Cleanup, Thrusts 1K, 1L, 1M, 1N, Biological Treatment of Explosives, Organics, Solvents, and Fuels in Contaminated Soils. The technical objectives are: i.) to describe, for different classes of compounds, the kinetics and endpoints of

biotransformations as functions of soil moisture, available carbon, and low temperatures and ii.) to elucidate the impact of rhizospheric zones on soil bioremediation potential.

Successful application of bioremediation at low temperatures requires knowledge of how freezing induced processes influence the pathways and rates of biologically mediated processes. Recent research indicates that at lower temperatures the interacting influences of moisture, soluble carbon, and temperature on microbial activity are unpredictable from data obtained at higher temperatures. Rate adjustments based on traditional approaches, such as scaling from laboratory studies or Q10 values obtained from higher temperatures, do not account for interacting phenomena encountered in field situations, and may not realistically describe processes governing bioremediation in soils exposed to severe or repeated freezing.

We have developed a system for measuring microbial activity at low temperatures and constant moisture potentials. A preliminary conceptual model is being developed from a series of laboratory experiments designed to integrate freezing and freeze-thaw influences on biological activity with chemical and physical processes. Field projects are in place to provide both authentic soil samples and field data. Freezing and freeze-thaw influences on biological, chemical, and physical processes will be integrated. Our approach will couple laboratory and field studies. Chemical structural activity relationships (SAR) will be used to select and group chemical classes of contaminants. Results will, therefore, be transferable based on structural activity relations rather than individual compounds.

Using rhizosphere effects to degrade organics is a promising, innovative technique which would be advantageous at many sites, particularly at remote locations where no feasible alternatives exist. The impact of low temperatures and extended or frequent freezing on the remediation abilities of these biological systems is unknown. Laboratory, growth chamber, and cold-room studies will transition into our ongoing field projects. Plants tolerant to seasonally frozen soil and having fibrous root systems will be selected to provide improved root distribution and root-soil contact. Enhanced root exudates may provide additional carbon that is frequently needed as a co-substrate for contaminant degradation. Root mycorrhizal associations will be promoted for their positive impact on phosphorus nutrition. Legumes will be exploited for their potential for mid-depth root penetration, nitrogen fixation capabilities, and resulting microbial stimulation in poor quality soils.

In accompanying field studies, larger native plant species, acclimated to specific geographic areas and climates, will be investigated for their ability to reach deeper depths, and to recycle soil moisture and associated mobile, solution-phase contaminants through the rhizosphere and towards the soil surface, zones of enhanced microbial activity.

This research differs from previous work in cold regions bioremediation because:

a. Private industry efforts have used biopiles, treatment cells, and similar technologies. These efforts are minimally monitored with limited on-site or laboratory analysis. Documentation is sparse and restricted. Freezing effects are not addressed although treatment systems are subjected to freezing.

b. EPA effort in EXXON Valdez cleanup was a coastal environment and subject to wave and storm action.

c. In-situ bioventing of lighter petroleum compounds (JP-4) in cold regions (Air Force) has focused on sub-surface, unfrozen soil systems. Improving our knowledge base may extend bioventing to environmentally acceptable use in the active zone of permafrost soils.

8. Expected Payoff:

Soil cleanup is required at military, federal, and civilian sites. Many sites are in cold, remote locations. The few alternatives that are available either use more costly, methods or incur liability due to non-compliance. Low input, scientifically defensible biotreatment alternatives would treat such sites at minimal cost, reduce or remove liability, and minimize clean-up associated damage to the site. The regulatory community is open to innovative biotreatment. The results from this research are dual use and would readily transition to the public sector through field research and demonstration sites that are part of CRREL's ongoing related projects. Increased knowledge would extend the operating season and potentially provide guidance for using natural freeze-thaw cycles advantageously.

Envisioned benefits include:

a. Application to the northern tier of the continental US to extend the biotreatment operating season.

b. In-situ treatment of contamination in the active zone of permafrost soils with minimal disturbance to fragile surface ecosystems, as well as application to the northern tier of the US.

c. Transition to Arctic and Sub Arctic sites, including Northern European and Former Soviet Union sites, where conditions, location, available infrastructure, and cost preclude more intensive technologies, is highly feasible.

d. Acquired knowledge would support a dual-use technology applicable to joint DOE-DoD soil-freezing containment technology by adding a cold-adapted bioremediation capability to soils contained by cryogenic barriers.

9. Milestones/Accomplishments:

1. Developed laboratory system for measuring soil microbial activity at low temperatures and controlled soil moisture potentials	06/93
2. Identified initial components of conceptual low temperature model	12/93
3. Evaluate importance of processes including rhizosphere effects	06/94
4. Evaluated importance of different chemical classes	12/95
5. Conducting field studies for comparison with laboratory results	06/96

6. Identify emergent-plant rhizosphere system in PCB soils 06/96
7. Manipulate field systems based on gained knowledge 08/96

The results from this project to-date suggest that rhizosphere-enhanced soil treatment can be used to remediate organic-contaminated soils at a significant cost savings. Rhizosphere-based treatment is applicable to permafrost and wetland soils, has a low initial cost, very-low operating costs, and can be favorably influenced by naturally occurring freeze-thaw and wet-dry cycles.

In laboratory studies using both legumes and grasses, we have measured increased microbial numbers and, more importantly, an increased percentage of the microbial population that were contaminant degraders, in rhizosphere soils relative to non-rhizosphere soils. Freeze-thaw cycles have stimulated microbial activity in soils. We have also demonstrated root growth into and through contaminated-soil zones in both cold-region soils and wetlands. We observed that root and plant growth could be inhibited and, in some cases, stimulated by soil contaminants. We have measured more a rapid decrease of selected organic contaminants in rhizosphere soil relative to non-rhizosphere soil. Freezing cycles caused a temporary decrease, and then an increase in contaminant degradation rates. A field study is underway in Fairbanks to compare rhizosphere treatment with other technologies.

10. Transition Plan:

Knowledge gained from this research will transition into related 6.2 projects, Low Temperature Biotreatment, Natural Remediation, and Biotreatment of Explosives in Cold Regions. Cold Regions Research and Engineering Laboratory (CRREL) is cooperating with WES on these work units.

The high cost of conducting research at actual field sites essentially precludes using research funding alone to support field testing, but the field experimental component is fundamental to realistic bioremediation research. CRREL's strategy has been to leverage research funds by partnering with State, Federal, and private sector cooperators who are involved in cleanup operations. CRREL is currently involved in field projects through partnering programs with Alaska Science and Technology Foundation, Alaska DOT&PF (CPAR), University of Alaska (CPAR), FAA, Air Force (Shemya and Elmendorf AFB), and private industry (Weston and Sampson Engineering, Inc., CPAR and RZA-AGRA, Inc., CPAR). These projects are primarily applied research and demonstrations; they provide authentic soil samples and field experimental sites, and facilitate laboratory-field communication. This approach also provides a real and highly visible avenue for transitioning and technology transfer, as demonstrated by our CPAR projects and cooperative projects with the Districts and Air Force. CRREL is also in the preliminary stages of developing additional cooperative field projects with private industry through CRADAs.

CRREL has coordinated transitioning with the a) Air Force, through the Engineering and Services Laboratory at Tyndall AFB and briefing the Center for Environmental Excellence at Brooks AFB on our projects. Additionally, CRREL has a cooperative project on Shemya Island through Elmendorf AFB; b) Navy, for future transitioning at the proposed Navy National Test Site and

c) EPA, through the Risk Reduction Engineering Lab., Cincinnati, OH, and Environmental Research Laboratory, Gulf Breeze, FL.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	500	700	220	200	1,620

12. Performers:

CRREL is uniquely well equipped for low-temperature research and the basic research will be conducted primarily at CRREL.

This research has been coordinated with Dr. D. Gunnison at WES, the lead laboratory for cleanup. CRREL will work with Dr. Gunnison at WES to maintain coordination with related research at WES.

A limited number of Universities have recently begun research in rhizosphere- based soil bioremediation. CRREL has discussed with the EPA the potential of involving Universities and intends to do so as appropriate. We have coordinated with the Air Force, Navy, and EPA to prevent duplication and facilitate cooperation.

Through Broad Agency Announcements, CRREL has developed partnerships with the University of Alaska, the University of Vermont, and the University of Arkansas to conduct this research.

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14. Keywords:

Bioremediation, Sub Arctic, Freeze, Cold, SAR, Rhizosphere

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Peroxone Treatment of Contaminated Groundwaters

3. **Lead Agency:** US Army

4. **Laboratory:** US Army Engineer Waterways Experiment Station (WES)

5. **Project ID:** #726

6. **Problem Statement:**

The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with explosives compounds. The current or traditional treatment technology available for use in explosives contaminated groundwater remediation is granular activated carbon (GAC). An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the very near future under the DoD's Environmental Quality and Technology Program (EQT). Remediation costs for both of these technologies fall within the $1.00 to $5.00/1,000 gallons range. UV/chemical oxidation is advantageous to GAC because it is a destruction technology and it does not produce a waste stream (i.e. spent GAC) requiring disposal. Also, unlike GAC, UV/chemical oxidation processes are still economically viable at relatively low groundwater concentrations. UV/chemical oxidation systems are often referred to as advanced oxidation processes because they result in the formation of powerful oxidizer species such as the hydroxyl radical ($OH^{\cdot}$).

DoD installations requiring remediation of explosives contaminated groundwaters will require that GAC or UV based chemical oxidation systems treat literally millions to billions of gallons of groundwater. The cost to the DoD alone will be extremely high. Many environmental engineers and scientists are hopeful that *in situ* technologies will one day completely replace pump-and-treat systems that use above-ground treatment systems. Unfortunately, the technical truth of the matter is that above-ground treatment systems will always have a place in groundwater remediation activities. *In situ* treatment technologies are not a panacea. Not all sites or site situations are capable of supporting an *in situ* treatment system. More cost effective, contaminant destruction, above-ground based treatment systems are required by the DoD.

Peroxone oxidation is a groundwater treatment technology that has great potential for treating contaminated groundwaters at reduced treatment costs. The main driving force in the development and presentation of this proposal is the potential cost savings that may be incurred with the fielding of this technology. Peroxone is a chemical oxidation process that has been used primarily for treatment of drinking water in both the United States and Europe. The process involves the addition of ozone (O_3) and hydrogen peroxide (H_2O_2) into a reactor system containing the contaminated groundwater. Peroxone generates hydroxyl radicals ($OH^{\cdot}$) through the reaction of ozone with hydrogen peroxide. Peroxone does not require the addition of

ultraviolet light to form radicals or destroy organic compounds. The hydroxyl radical is a powerful oxidizer that can destroy organic compounds into environmentally safe compounds. The stoichiometric reactions that result in the generation of the radical during peroxone treatment are listed below,

$$H_2O_2 + H_20 \rightarrow HO_2^- + H_30^+$$
$$O_3 + HO_2^- \rightarrow OH + O_2^- + O_2$$
$$O_2 + H^+ \rightarrow HO_2$$
$$O_3 + O_2^- \rightarrow O_3^- + O_2$$
$$O_3^- + H^+ \rightarrow HO_3$$
$$HO_3 \rightarrow OH^\cdot + O_2$$

Since the process does result in the formation of radicals, it is considered an advanced oxidation process (AOP). Actual cost information obtained from French engineers indicate treatment costs as low as \$0.02 to \$0.10 per 1,000 gallons treated (for dilute concentrations) have been reported. This represents an order of magnitude reduction in remediation costs as compared to traditional technologies such as activated carbon and traditional UV based AOPs. Since peroxone does not require UV addition, operational problems associated with fouling of the quartz sleeves housing UV lamps or poor groundwater UV transmissivity are not of concern; thereby, eliminating a big operational concern and expense associated with UV based oxidation processes.

This work unit will support unfunded components of the DoD STRAT Plan and will meet or partially meet several DoD user requirements. These requirements are:

Technology for removal of energetics/other organics contamination.
Treatment system for water contaminated with organic contaminants.
Treatment of Navy revellent contaminants in salt/brackish/groundwater matrices.
Isolation and treatment technology for contaminated surface water impoundments.
Decontamination of soils containing energetics materials.
Contamination under buildings and roads.
Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
Decontamination of soils containing energetic materials.

7. Project Description:

The WES has evaluated the use of peroxone processes for treatment of explosives contaminated groundwaters using bench scale peroxone reactors. Experiments using laboratory prepared solutions of TNT-distilled water have indicated that peroxone has similar removal kinetics to traditional UV based AOPs. WES, working with Mr. Randy Cerar, Army's Environmental Center (AEC), has evaluated peroxone for treatment of contaminated groundwaters from Milan Army Ammunition Plant (AAP) and Cornhusker AAP with the results being very encouraging. WES and Rocky Mountain Arsenal (RMA) have determined that peroxone has a high potential

for treating groundwaters contaminated with a variety of other contaminants. Estimated costs fall within the $0.10 to $0.80/1,000 gallons treated range. WES has also performed studies using sonolytic catalyzation indicating that the addition of ultrasound may dramatically enhance oxidation reaction rate. In summary, bench efforts performed by WES indicate that peroxone processes are ready for evaluation at DoD installations using pilot scale equipment.

The overall objective of this project is to accelerate development of peroxone oxidation processes for treatment of explosives contaminated groundwaters. Process feasibility will be evaluated at both the bench and field pilot scale, with particular emphasis placed on-site pilot studies. The objectives of this project will be approached through performance of a series of research tasks. These tasks are listed and discussed below:

Task I. Determination of Reaction Pathways and Kinetics. Other funding sources will be used by WES to determine reaction pathways of explosives parent compounds. This effort will investigate oxidation pathways of environmental explosives by-products, such as amino-toluenes, which are typically found in explosives contaminated groundwaters. Since peroxone is a destruction technology, determination of the predominant oxidation pathway of selected explosives environmental by-products will be determined using laboratory solutions of buffered distilled water and reagent grade target chemicals. Only single solute solutions will be used so additional carbon sources do not interfere with pathway determination. Kinetic parameters (at minimum, peuso-first order rate constants) will also be determined. Analytical methods to be employed in determination of treatment pathways and kinetics will include high performance liquid chromatography (HPLC), stopped-flow spectrophotometry, and gas chromatography (GC).

Task II. Selection and Shipment of Groundwater Samples. Actual groundwater samples from contaminated DoD sites will be used in both the bench and pilot scale studies. This will ensure that the study remains focused on rapid field implementation. Candidate sites include Milan Army Ammunition Plant, Cornhusker Army Ammunition Plant, Volunteer Army Amunition Plant (National Test Site), and a former Nebraska Ordnance Plant. Samples will be collected and shipped to WES for the bench scale studies. NOTE: All pilot studies will be performed on-site. Results from the bench testing will be used to design comprehensive pilot studies at a minimum of at least two DoD sites. Obviously, site groundwater samples used in the bench study will be carried through to the pilot level of effort.

Task III. Bench Scale Studies. Bench scale studies will be performed to determine process feasibility, verify reaction kinetics and oxidation pathways, estimate initial treatment cost estimates, and set pilot studies test matrices. The bench studies will be performed using one liter all glass reactors operated in semi-batch mode with respect to ozone application. Groundwater samples from various candidate pilot study sites will be evaluated in this study task. These studies will be performed at chemical oxidation laboratory of the Hazardous Waste Research Center (HWRC) located at the USAE Waterways Experiment Station (WES). These studies will also investigate the feasibility of integrating ultrasonic catalyzation as a means of enhancing contaminant oxidation rate and improving mass transfer limitations. If feasible, a CRADA with a reputable ultrasound process equipment manufacturer will be initiated for collaboration in terms of adding sonolytic catalysis to the pilot system.

Task IV. Pilot Scale Studies. Pilot scale studies will be performed using a mobile pilot peroxone system with .5 to 10 gallon per minute operating range referred to herein as the WES Peroxone Oxidation Pilot System (POPS). Four all-glass columns plumbed in series will serve as multiple contact chambers. The system will include several automated process operations and data collection systems that will be used to fully evaluate process feasibility in the field. At least two sites containing groundwater contaminated with explosives will be treated using the pilot system. This task will verify the results derived from the bench studies, evaluate process equipment, and refine cost estimates. The WES will perform these activities with AEC and COE Omaha providing site management and technical support.

Task V. Draft Applications and Design Manual. An applications manual in the form of a WES report will be drafted by WES, US Army Corps of Engineers (COE)-Omaha District, and COE-Missouri River Division (MRD) for use by the user community in designing and fielding the technology. It is believed that inclusion of the design user community (COE) early in process development will ensure development of a useful and easily transferable product. Key issues to be included in the design manual are:

1. Techniques for performance of bench scale peroxone treatability studies - This information will ensure that engineering firms under contract to the installations and COE district offices will be able to properly evaluate peroxone during the FS stage of site remediation. The research team for this proposal will be available for consultation at any time during full field implementation to ensure a smooth transition of the technology from the research and development community to the user community.

2. Process feasibility and potential limitations - One important factor in development of any technology is a firm understanding of the limitations of the technology. The manual will detail all limitations and short-comings associated with implementation of peroxone that are identified. Close coordination with the full user community will be maintained during the full-field application stage to further identify any additional limitations and problems as they occur. It is believed that the manual should be a "living" document that is periodically updated to ensure that corporate memory (DoD) is not lost during implementation at various sites. Lessons learned, whether good or bad, must be recorded so that other installations attempting implementation are keep fully abreast of new technical developments in order to ensure a higher potential for successful implementation at reduced costs compared to existing technology. Particular emphasis will placed on ensuring that this information is added to various prominent technology bulletin boards.

3. Results from the bench and pilot studies - The results of both the bench and pilot studies will be presented in a concise and applications oriented manner. These results will be further transmitted to the user and regulatory communities. It is important that the regulatory community is completely confident that peroxone can be safely applied at DoD sites.

4. Summarize cost estimates and full scale equipment availability - The manual will also include full cost estimates based on the results of both the Rocky Mountain Arsenal (RMA) and EQT/SERDP demonstrations. An assessment of available equipment will be included to assist

the design engineer in equipment selection. Basically, all equipment required for peroxone implementation are already available due to its operational history within the drinking water industry and relative simplicity in terms of equipment requirements. The assessment of equipment will be oriented toward hazardous waste site remediation and the particularities associated with this unique technical and regulatory arena.

As stated above, the implementation manual will be very design and applications orientated. The manual will serve as a handbook for implementation of peroxone at other field sites. Peer review from other agencies such as the USEPA laboratories and other COE design centers will be coordinated. Potential collaboration with the USEPA's SITE Program will be pursued by WES.

Key technical issues to overcome as identified to date are listed below:

a. Ensure that the parent explosives and amino based environmental byproducts are oxidized into environmentally safe, non-regulated (benign) compounds.
b. Determine if peroxone can effectively treat contamination levels typically found at DoD/Doe installations as opposed to organics levels that have traditionally associated with drinking water (which is what peroxone was originally developed for).
c. Determine the impacts of complex contamination matrices on treatment predicted from kinetic models.
d. Determining the economics and scale-up potential of ultrasound systems.

8. Expected Payoff:

The DoD has numerous sites that contain groundwaters contaminated with explosives. The existing technology, activated carbon adsorption, is costly, does not destroy the explosives, and results in the production of spent carbon which may pose a disposal problem. The WES has recently completed evaluation of traditional ultraviolet (UV) based chemical oxidation processes for treating explosives contaminated groundwaters. AEC plans to demonstrate these processes in FY94. The cost of traditional UV based oxidation processes is expected to range from $1.00 to $5.00/1,000 gallons of water treated. This is the same cost range experienced with activated carbon adsorption systems; however, chemical oxidation is much more flexible, is a destruction process, and produces no residuals requiring disposal. Peroxone processes are expected to costs in the $0.10 to $8.00 range, which represents potentially a full order of magnitude in cost savings over both activated carbon and traditional UV based chemical oxidation processes. The expected ease of system design and operational flexibility over the other chemical oxidation processes make this process appear extremely promising.

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. Peroxone treatment will economically fill a gap that currently exist in terms of treatment of low level contaminated groundwaters. Although no funding is requested for the RMA pilot studies evaluating DIMP, pesticides, and aromatics removal, performance of this work unit will improve the overall quality of the RMA study by allowing RMA/WES to use an improved pilot system then could be developed on the RMA budget alone. In return, the RMA pilot studies (FY94) will allow for

evaluation of the POPS unit in terms of mechanical performance prior to performing the explosives pilot studies in FY94-96. Potential research agreements with the private section (CRADAs) will also be investigated to ensure rapid transition to the user community.

9. Milestones/Accomplishments:

1. Complete first bench scale evaluation	07/94
2. Complete construction of pilot unit	05/94
3. Perform RMA pilot study	08/94
4. Perform first pilot study	08/95
5. Perform second pilot study	06/96
6. First draft of design package	02/96
7. Final design package	09/96

All three pilot sites have been selected (Cornhusker, Nebraska-OP, and Volunteer AAP, LA). Two of the three bench studies have been completed (Cornhusker and Nebraska-OP). The results from the Cornhusker study are very encouraging. We continue to work with AEC to demonstrate this promising technology. Presented at the 1995 AICHE Summer National Meeting, "Treating Contaminated Groundwater Using a Peroxone Oxidation Pilot system".

10. Transition Plan:

After pilot scale evaluation of the technology is complete, transition to the user community will be accomplished through various technical reports, publications, briefings, and conference presentations. Interfacing with COE-MRD through this project partnership should accelerate transition of the technology into COE activities, while the USEPA, DOE, and USAF will be briefed periodically on the progress of this effort to ensure smooth transition into their programs. It is fully anticipated that the technology developed under this effort will be directly applicable toward other organic contaminants that are a major concern of these agencies. Once the pilot studies at the explosives contaminated sites have been completed, additional partnering with these agencies can be initiated for evaluation of peroxone for treatment of groundwaters contaminated with other organic compounds such as chlorinated solvents, fuels, and wood preserving wastes using the WES POPS unit.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	570	950	180	496	2,196
WES	400	350	100	100	950
CRREL	200	200	50	0	450
AEC	0	150	80	100	330

12. Performers:

The WES will have the technical lead on this project. The US Army Engineer Cold Regions Research and Engineering Laboratory (CRREL), Dr. Tom Jenkins, will provide chemistry expertise toward identification of potential intermediates of incomplete oxidation. Mr. Ted Streckfuss, US Army Corps of Engineers-Omaha District and Mr. Lindsey Lien, COE-Missouri River Division, will develop a process design package and provide design concern input to ensure that the products of this effort can be easily utilized by and are of benefit to the user community. Messrs. Randy Cerar and Richard O'Donnell, US Army Environmental Center (AEC), will assist WES with the Army facility pilot study(s). Ms. Carmen Lebron, US Naval Facilities Engineering Services Center (NFESC), will also participate in this study by assisting WES in providing information on on-going UV/ozone field efforts.

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14. Keywords:

Peroxone, Explosives, Groundwater, Advanced Oxidation Processes, Pilot Study, Oxidizers

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Bioremediation of Hydrazine

3. **Agency:** U.S. Air Force

4. **Laboratory:** Armstrong Lab

5. **Project ID:** #118

6. **Problem Statement:**

Current method for hydrazine spill decontamination is the addition of oxidizers such as sodium hypochlorite, hydrogen peroxide, UV-chlorination, and/or ozone. The results of the oxidation reaction have shown the production of hazardous conditions or even more toxic compounds, which further contaminate the environment. An alternative disposal method is incineration that liberates hydrocarbons and soot into the atmosphere, producing significant quantities of air pollution and residual wastes. A treatment technique needs to be developed to replace existing disposal options, emergency spill situations, and address environmental contamination from past disposal activities of these materials. Biological treatment techniques offer the most cost-effective alternative to meet these needs.

7. **Project Description:**

The approach for successful implementation of this biotechnology will involve process discovery, determination of limiting factors, and scale-up of the biological system. This will include bench-scale testing to optimize a biological catalyst to be followed by field implementation at a contaminated site. The bench-scale work will measure the redox potential of the biological catalyst (diazoluminomelanin) against that of the clay catalyzed reactions. Column-slurry tests will be conducted to determine in situ biodegradation capability and optimize remedial design parameter factors. The fate of hydrazine and the transport of the environmental reaction/decomposition products will also be studied during this research effort. Toxicology studies will provide a systemic approach to a remediation technique, and provide a risk assessment tool. A pilot demonstration will be conducted with appropriate controls at field scale to provide a design and cost feasibility report.

8. **Expected Payoff:**

This project will produce a cost-effective, more efficient, destructive process to cleanup hydrazine spills and remediate sites contaminated with hydrazine and its derivatives within regulatory requirements. An understanding of the environmental fate and transport of hydrazine spills will provide a target for the remediation technique. Toxicology studies will insure that the remediation technique will remain within regulatory compliance following spill treatment.

9. Milestones/Accomplishments:

1. In-house Literature Evaluation and Review	10/94
2. Perform Bench-Scale Redox Testing	12/94
3. Perform Fate and Transport Work	03/95
4. Perform Toxicology Studies	12/95
5. Complete Redox Chemistry Work	11/96
6. Develop Pilot-Scale Bioreactor System	11/96
7. Complete Fate and Transport Work	03/97
8. Initiate Field Testing	11/97
9. Complete Field Demonstration	02/99
10. Report Results	06/99

Upon completion of the literature and technology review, a plan was established to develop a hydrazine spill bioremediation technique. Initial benchscale biocatalyst studies were performed showing the destruction of neat hydrazine fuels by a biocatalyst (diazoluminomelanin). Hydrazine environmental fate studies identified and quantified valuable reaction and decomposition products. This knowledge will provide vital endpoints for the remediation technique.

10. Transition Plan:

Near term products of this technology endeavor will be technical reports and professional publications to keep government R&D agencies and their contractors informed of our progress. Once the technology is validated, design guidance and cost data will be distributed to the service agents/contractors and environmental quality technical synopsises will be submitted to the MAJOM's. This project will transition to the Air Force Environmental Systems Program Office (HSC/YAQ) and the Air Force Center for Environmental Excellence (AFCEE).

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	420	0	555	350	700	2,025

12. Performers:

This effort will be managed by Lt. Kuch at the Environics Directorate of Armstrong Laboratory (AL/EQ). This project teams world renown scientists, tops in their respected fields of study, working to develop a hydrazine remediation technique. The development of the bioremediation technique (DALM) will be conducted by Dr. Jonathan Kiel of the Occupational and Environmental Health Directorate of Armstrong Laboratory (AL/OE). The hydrazine environmental fate studies were performed by Dr. Pat Sullivan at the University of Wyoming. Hydrazine breakdown toxicology studies will be performed by Dr. Bantle at Oklahoma State University.

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14. Keywords:

Bioremediation, Biodegradation, Hydrazine, Biocatalyst, Diazoluminomelanin (DALM), Environmental, Toxicological, Decomposition

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Bioremediation of Energetic Materials

3. Agency: Air Force

4. Laboratory: Armstrong Laboratory/Environics Directorate

5. Project ID: #886

6. Problem Statement:

The Department of Defense (DoD) has identified over 1200 explosive contaminated sites. A biological process needs to be developed to effectively degrade nitroaromatic compounds into environmentally benign compounds. A wide variety of sites in Europe and the United States, where explosives have been produced, are extensively contaminated with dinitrotoluene (DNT). The contamination consists of a mixture of 2,4-DNT and 2,6-DNT in a ratio of four to one. Armstrong Laboratory researchers have discovered microbial strains that completely biodegrade 2,4-DNT aerobically. However, the same microbes are unable to degrade 2,6-DNT. Not only is 2,6-DNT nonbiodegradable, but the compound inhibits the degradation of 2,4-DNT. Therefore, the microbial inhibition of 2,6-DNT must be overcome in the development of a soil and groundwater remediation technique. In accordance with DoD Project Reliance, the Armstrong Laboratory/Environics Directorate's (AL/EQ) in house nitroaromatic research results will transition to the US Army Engineer Waterways Experiment Station (WES) for further development.

7. Project Description:

In order to overcome the inhibition of 2,6-DNT, the degradation of the energetic material will be studies in two efforts. AL/EQ researchers will attempt to overcome the inhibition through aerobic mechanisms. A second effort at the Fraunhofer Institute, Stuttgart, Germany, will involve overcoming the inhibition anaerobically. Laboratory bench-scale fluidized-bed reactor studies will apply the results of the inhibition studies. Process scale-up will include field fluidized-bed reactor studies at Volunteer Army Ammunition Plant, TN, which has DNT contaminated groundwater.

8. Expected Payoff:

The project will produce a destructive bioremediation process for nitroaromatic compounds. The results of this project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.G: Treatment Technology for Explosives in Groundwater, and also Requirement Thrust 1.K: Treatment technology for Explosives in Soils. Additionally, complete transition of USAF basic and exploratory nitroaromatic research to US Army of Project Reliance.

9. Milestones/Accomplishments:

1. Upgrade Bioreactor	06/95
2. Conduct Lab Inhibition Studies	11/95
3. Complete Lab Inhibition Studies	05/96
4. Perform Lab Fluidized-Bed Reactor Studies	06/96
5. Complete Lab Fluidized Bed Reactor Studies	11/96
6. Perform Field/Pilot Reactor Studies	12/96
7. Complete Field Studies	10/97
8. Publish Final Report	01/98

The bioreactor to be utilized in the field demonstration has been upgraded. An aerator (bubble contactor) and a dissolved oxygen (DO) meter were added to the bioreacter, to improve system performance. Preliminary laboratory research is investigating the source of the microbial inhibition. Early results have identified microbial isolates with the potential ability to overcome the inhibition of 2,6-DNT

10. Transition Plan:

The results of bench-scale and field demonstrations will transition to WES for further development. The developed bioremediation process will complement the Army's research endeavors, and add another soil and groundwater remediation "tool" to the US Army's nitroaromatic remediation "tool box". Ultimately, the final results of the field demonstration will transition to the AEC for full-scale validation.

11. Funding: $(K)

FY96	FY97	TOTAL
100	480	580

12. Performers:

This effort will be managed by Lt. Kuch at the Environics Directorate of Armstrong Laboratory (AL/EQ). This project teams world renown scientists, tops in their respected fields of study, working to develop a hydrazine remediation technique. AL/EQ researchers, under the guidance of Dr. Jim Spain, will attempt to overcome the inhibition through aerobic mechanisms. A second effort will involve overcoming the inhibition anaerobically by Dr. Knackmuss at the Fraunhofer Institute. A USAF/US Army collaborative field demonstration will apply laboratory knowledge in the filed. Dr. Mark Zappi (WES) will spearhead the field demonstration at Volunteer Army Ammunition Plant, TN. During the field demonstration, AL/EQ researchers will provide scientific guidance in the areas of microbiology, biochemistry, and genetics.

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14. Keywords:

Bioremediation, Biodegradation, Energetics, Nitroaromatic, Dinitrotoluene, Bioreactor, Environmental, Microbial, Groundwater, Soil, Contamination

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Catalytic In Situ Treatment of Chlorinated Solvents

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Laboratory

5. **Project ID:** #107

6. **Problem Statement:**

Organic liquids, such as chlorinated solvents, nonchlorinated solvents, and fuels, have been used in massive quantities over the last four decades. Release of these liquids to the environment accounts for a significant portion of environmental contamination requiring cleanup. These contaminants have migrated through the subsurface and entered groundwater at over 2,000 DOD sites. There is a comparable degree of contamination at DOE and private Superfund sites.

The limiting factor to satisfactory remediation at over 75 percent of the hazardous waste sites in the United States is restoration of groundwater quality. The technology chosen at over 90 percent of the sites with contaminated groundwater is extraction followed by surface treatment. This technology, commonly known as pump-and-treat, contains contaminant plumes and removes dissolved-phase contamination in relatively homogeneous geologic formations. As a result of the slight solubility of the contaminant into the surrounding groundwater, and sorption to aquifer materials during transport, pump-and-treat processes require the treatment of massive amounts of water to remove relatively little contamination. Estimates of the duration of pump-and-treat necessary to fully remediate contaminated sites range from decades to centuries.

The high cost of pump-and-treat technologies are due to operations and maintenance costs, including energy for pumping and water decontamination, materials for treatment, and labor for constant operation of the process. A newly-developed process, called funnel-and-gate, is an in situ technique which directs contaminated groundwater under passive flow through an engineered subsurface region for decontamination. While this process may not reduce the duration of treatment, once installed, it will operate with little or no operating and maintenance (O&M) investment, resulting in considerable savings over the life of the project.

The best test of this technology will be in a well-characterized aquifer, treating a well-characterized plume. An accurate mass balance can be obtained only when the plume results from a controlled release of pollutant. The Air Force was recently awarded a SERDP grant to construct just such a controlled release site, which will be used for this demonstration. The groundwater can be decontaminated by a number of chemical, physical, biological, or a combination of methods. Existing research projects at both Armstrong and Athens (EPA)

Laboratories have identified treatment methods which are well suited to funnel-and-gate deployment.

7. Project Description:

The funnel-and-gate consists of low hydraulic conductivity cutoff walls with gaps that contain in situ reactors (such as reactive porous media), which remove contaminants by abiotic or biological processes. The cutoff walls (the funnel) modify flow patterns so that groundwater flows primarily through high conductivity gaps (the gates). Groundwater plumes are thus directed through the in situ reactors in the gates where physical, chemical or biological processes remove contaminants from groundwater. Remediated groundwater exits the downgradient side of the reactor.

This applied research program will develop guidance on the use of funnel and gate systems containing various reactive media to treat chlorinated solvents in groundwater. Studies will address two critical unknowns: 1) hydrogeologic uncertainties that have led to at least one failure of the technology, and 2) chemical reactions between reactive media and contaminants that lead to better designs. These studies will lead to a rigorous pilot-scale field demonstration to prove the technology. An understanding of site-specific hydrogeology is critical to the design of funnel and gate systems. Groundwater flow rates and pathways must be known to position gates and to design the amount of reactive media required. New or improved groundwater flow and transport models will be developed to ensure that designers understand the system they will treat.

The proposed research will apply hydrogeological principles and aquifer modeling techniques to develop the most efficient designs and methods for construction of the walls. An increased understanding of groundwater flow through the engineered systems will allow for the most frugal emplacement while ensuring complete capture of the contaminant plume. The proposed work will develop new (or modify existing) three-dimensional groundwater flow models to simulate the flow of groundwater and contaminant plumes through aquifers modified with funnel and gates. Of particular interest will be the influence of aquifer heterogeneities and site characterization. Variables to be examined will include size and shape of the funnels, requirements for wall integrity, number and placement of gates, and groundwater velocity through the gates. New modeling techniques will be developed to account for effects like aquifer clogging by iron bacteria. The models will be verified in field demonstrations using nonhazardous tracers to monitor groundwater movement through the system.

Concurrently, gate technologies will be designed and scaled for use with funnel-and-gate configurations. The Armstrong Laboratory Environics Directorate has for several years been investigating abiotic dechlorination in order to develop in situ treatment processes. Other research has been directed at contaminant mobility reduction using surfactants, a process which may enhance biological treatment in gates. The Environmental Research Laboratory at Athens has been studying abiotic dechlorination using elemental iron, enhanced with sulfur compounds, as an in situ process. All of these processes can potentially be used as gates to treat groundwater contaminated with chlorinated solvents. The elemental iron/sulfur catalytic dechlorination system developed by the Athens Laboratory is proposed as the first demonstration gate. Regardless of

the nature of the gate, pathway analyses must be conducted in the field and laboratory, not only to predict residual toxicity, but also to aid in deriving the optimum design configuration. Mass accounting must be fully balanced to ensure complete destruction of the contaminant. Where necessary, labeled compounds and tracers will be used. Coordinating the hydrogeologic modeling project with further development of the gates, a fully integrated system can be installed and tested in the field.

The proposed work addresses Thrust 1H: Treatment of Solvents in Groundwater, and Thrust 1I: Treatment of fuels in Groundwater under Pillar 1: Cleanup, of the Tri-Service Strategic Environmental Research and Development Program. Failure of innovative technologies at a regulated site would result in wasted cleanup dollars and may actually complicate subsequent cleanup. Proving technologies in a well-controlled, isolated site will limit the risk and possible damage resulting from failure.

8. Expected Payoff:

Most contaminated sites currently undergoing pump-and-treat remediation are expected to be tractable to funnel and gate configurations. Installation of passive treatment zones will save on O&M costs for what will likely be decades of continued treatment. With no active pumping involved in the process, these systems may be installed at sites for which power utility installation is a formidable obstacle to installation of pump-and-treat systems.

9. Milestones/Accomplishments:

	Date
1. EPA report on the mass balance of iron/iron sulfide reaction	06/95
2. Report on the dehalogenase enzyme reaction and plant sources for TCE and PCE	12/95
3. 3-D modeling interim report	01/96
4. Guidance documents on designing funnel and gate systems	01/96
5. Remedial Action Cost Engineering and Requirements	03/96
6. 3-D modeling final report	03/96
7. Design funnel-and-gate hydrology demonstration	05/96
8. Install demonstration system	07/96
9. Collect and analyze operational and monitoring data	04/97
10. Final report	09/98

Armstrong Laboratory Environics Directorate and the EPA Athens Laboratory: Four reactor columns were simultaneously run for the conversion of 50 uM TCE in water. The columns were packed with different materials to investigate the conversion efficiency variations. In all cases, a significant conversion of TCE was observed. A process design protocol for the application of granular iron/pyrite mixtures to groundwater remediation was developed. Treatability studies are being designed for Massachusetts Military Reservation and Dover AFB. A sediment dehalogenase was isolated, and the reaction mechanism is being studied. The enzyme can dehalogenate HCA, PCE, TCE, DCE, and vinyl chloride, and react with ethylene. Results of this

work were featured in the July 1995 cover story, "Groundwater Cleanup, Zero-Valent Metals Offer New Way to Remove Contaminants", in Chemical and Engineering News.

Modeling research for funnel-and-gate applications was conducted by the University of Waterloo (contract effort): One dimensional test cases were completed using the PC-based SPH analysis code, GROWFLOW. GROWFLOW is now ready for testing. Analytical models consisting of a contaminant transport model and a hydraulic model have been completed.

The design of an In Situ Hydrogen Peroxide Generation Demonstration was conducted by SRI International (contract effort): The purpose of this research is to develop a protocol for using hydrogen peroxide in the gate of a funnel-and-gate system to degrade groundwater contaminants. To date, SRI has evaluated different iron oxides as catalysts and the conditions under which the oxidation of an organic contaminant was optimized. They have also performed initial tests to establish an experimental hydrogen peroxide concentration for use as a baseline in the optimization study.

Delta Research Corp was contracted to produce a Remedial Action cost Engineering and Requirements (RACER) System Modification for Funnel-and-Gate Groundwater Remediation. This model will provide cost and economic analysis to identify the relative cost effectiveness of competing funnel-and-gate remediation technologies. Delta has submitted a Draft Concept Paper and a Model Development Plan for review. Review comments from AL/EQW and EPA were consolidated and returned.

The Armstrong Laboratory Environics Directorate and the EPA Athens Laboratory are both active participants in the Remediation Technologies Development Forum's (RTDF) Permeable Barriers Working Group. The Air Force and EPA formed this workgroup with E.I. DuPont de Nemours and Co., Dow Chemical Company, General Electric, Monsanto, DOE Savannah River Laboratory, DOE Sandia National Laboratory, Rust Geotech , U.S. Bureau of Mines, and the University of Waterloo with the goals of crossfeeding permeable barrier technologies and standardizing procedures for conducting technology demonstrations and monitoring their performance. The group plans to conduct one (or more) definitive demonstrations of in situ zero-valent iron reduction of TCE/PCE and other chlorinated solvents in groundwater. Sub-groups have been established to make recommendations on Treatability Studies, Barrier Emplacements, Performance Monitoring, and Modeling.

10. Transition Plan:

The reports and guidance documents resulting from this work will be written such that they will be suitable for planning implementation at scales larger than the field studies of this project. The Air Force Environmental Systems Program Office (HSC/YAQ) and the Air Force Center for Environmental Excellence (AFCEE/ES) will further develop the technical information obtained from this research and apply it to full-scale remediations and finalization of the technical data package. A preliminary principles of practice manual, technical reports and professional publications will be produced for distribution to the appropriate technology transfer offices of the Air Force, Army, Navy, DOE, and EPA. Technologies developed by this project will also be

transitioned to other federal agencies and industry by the RTDF Permeable Barriers Working Group.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	735	0	550	990	850	3,125

12. Performers:

The performers for the proposed work are US Air Force Armstrong Laboratory, Environics Directorate, the EPA Environmental Research Laboratory at Athens, and the University of Waterloo, Waterloo, Ontario, Canada.

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14. Keywords:

Funnel and Gate, Remediation, Cleanup, Aquifer, TCE

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Joint US/Germany In-Situ Bioremediation Demonstration

3. **Agency:** U.S. Air Force

4. **Laboratory:** Armstrong Laboratory

5. **Project ID:** #99

6. **Problem Statement:**

The goal of this effort is to conduct a field demonstration of bioventing concurrent with two groundwater treatment strategies at a JP-4 jet fuel contamination site at Rhein Main Air Base (AB), Germany. The results generated from this field project will assist in successfully transferring these technologies to the German regulatory authorities and the German environmental consulting firms working on U.S. military base cleanup activities in Germany.

There are approximately 2,000 fuel/hydrocarbon contamination sites the US Air Force must address in it's Installation Restoration Program. There are also numerous such sites at military facilities throughout Germany and other NATO countries. Any in-situ method for soil or groundwater cleanup will offer huge cost savings over the currently used ex-situ disposal or treatment methods.

This effort represents an enhancement to several existing Air Force Science and Technology projects: "Bioventing for In-Situ Cleanup of JP-4 Contaminated Soils," "Anaerobic Degradation of Fuel-Contaminated Groundwater," and "Natural Attenuation for Hydrocarbon Fuels."

7. **Project Description:**

The technical objective of this effort is to demonstrate bioventing for the cleanup of JP-4 contaminated soil located in the fuel storage/transfer area at Rhein Main AB Germany. To improve the effectiveness of bioventing, the "bioslurper system" will also be demonstrated to remove floating product from the site prior to bioventing. The rationale for using natural attenuation to address the contaminated groundwater will also be tested at a separate JP-4 contamination site at Rhein Main AB. Specific technical tasks are outlined below.

Concurrent with this project will be a study of in-situ soil and groundwater petroleum hydrocarbon cleanup technologies by the University of Karlsruhe, Germany. Karlsruhe University researchers will conduct a field study of a technology similar to bioventing for contaminated soils and an active bioremediation technique (nitrate enhancement) for the contaminated groundwater. These studies will be conducted adjacent to the American bioventing study at the fuel storage/transfer area on Rhein Main AB.

The technical approach will include construction of the experimental plots and outfitting with the necessary hardware and monitoring equipment. To the extent possible, these tasks will be accomplished jointly by the Armstrong Laboratory (AL) contractor and the University of Karlsruhe researchers. The mechanism which facilitates this international collaboration is the DoD US-German Data Exchange Agreement Annex DEA-A-94-GE-1521.

This work will assist the DoD in achieving its Year 2000 cleanup goals and also be applicable to similar fuel contamination sites on DOE facilities. The proposed effort relates closely to AF, Navy, and EPA's previous and ongoing work in bioventing and natural attenuation. AL/EQ and the US Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory are also currently involved in development of nitrate enhancement for groundwater decontamination as are a few select researchers in Germany.

The technical risk is low. These technologies have been successfully demonstrated in the United States. Innovative German sampling, analysis, and monitoring techniques will be incorporated in the Armstrong Laboratory portion of the study.

This project directly contributes to the objectives identified in the DoD's Tri-Service Environmental Quality R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.L Solvents/Fuels Contaminated Soils.

8. Expected Payoff:

The bottom-line payoff is that these very low-cost technologies will save the US and German governments millions of dollars per contaminated site over conventional cleanup technology. The key outcome of this joint demo will be performance and cost information to convince the German regulatory authorities that bioventing/bioslurper/natural attenuation are viable treatment options for hydrocarbon contaminated aquifer material. Another outcome will be comparative side-by-side performance information on the different U.S. and German clean-up technologies. The bioremediation techniques, independently developed by the U.S. and Germany, could be enhanced as a result of sharing unique sampling, analysis, and monitoring techniques. This could further lower the cost of these already very cost-effective technologies.

9. Milestones/Accomplishments:

	Planned	Completed
1. Draft Treatment Study Test Plan		12/95
2. Final Treatment Study Test Plan		1/96
3. Construction of Experimental Field Plots	02/96	
4. Initiation of U.S. Bioventing Test	02/96	
5. Completion of All Field Experiments	10/97	
6. Draft Technical Report	10/97	
7. Final Technical Report	12/97	

10. Transition Plan:

Technical results from this demonstration will be transferred via interim reports throughout the life of the project, final technical report, and design guidance. Design packages, technical data, and operator manuals will be available and will be transitioned to the Air Force Center for Environmental Excellence (AFCEE) for implementation into existing manuals on bioventing and natural attenuation, to HQ USAFE/CEV for implementation at Air Force sites throughout Europe and to the appropriate Army, Navy, AF, DOE, and EPA technology transition offices.

The users (contracting and consulting firms such as Battelle) will be the performers. The main coordination needed will be with the German regulators to keep them informed of the project's progress. The industries ability to assume production is high.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	250	200	200	300	950

12. Performers:

The project will be jointly managed by the Environics Directorate of Armstrong Laboratory (AL/EQ) and the German BWB through our existing Data Exchange Agreement. It will be performed by Battelle Memorial Institute (AL/EQ IQIQ contractor) and the University of Karlsruhe, Germany. No CRADAs are anticipated.

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14. Keywords:

Bioremediation, Natural Attenuation, Bioventing, Remediation, Cleanup, Nitrate Enhancement, Petroleum Hydrocarbons, Fuel, Bioslurping, Free Product, Floating Product

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Aquifer Restoration by Enhanced Source Removal

3. **Agency:** Environmental Protection Agency

4. **Laboratory:** National Risk Management Research Laboratory

5. **Project ID:** #368

6. **Problem Statement:**

The goal of this project is to provide field demonstrations of innovative processes to remediate aquifers contaminated by non-aqueous phase liquids (NAPLs) including fuels, solvents, and other organic contaminants in a timely and cost-effective manner. These demonstrations are targeted at DoD, DOE, EPA, their contractors, and other public and private organizations responsible for remediation of contaminated ground water. Low-solubility organics such as chlorinated solvents were used and released to the environment in massive quantities during the 1950's, 60's and 70's. These contaminants have migrated through the subsurface and entered ground water at over 2000 DoD sites. At these sites the organic contaminants are found in one of three phases: (1) dissolved in the ground water (dissolved phase), (2) sorbed to the aquifer solids (sorbed phase), or (3) as a separate non-aqueous phase liquid (NAPL phase), all of which need to be removed if the ground water is to be restored to a usable quality.

The limiting factor to satisfactory remediation at over 75 percent of the hazardous waste sites in the United States is restoration of ground-water quality. For those contaminants that have found their way into ground water in the deeper subsurface, remediation technology options are extremely limited. The technology chosen at over 90 percent of ground-water contaminated sites is extraction followed by surface treatment. This technology, commonly known as *pump-and-treat*, has had some success in containing contaminant plumes and removing dissolved-phase contamination in relatively homogeneous geologic formations, but, as currently implemented, has not proved to be effective at restoring contaminated ground water to desired levels of cleanliness. The major limitations to the successful use of pump-and-treat are related to difficulties in extracting contaminants from the subsurface. Aquifer characteristics important in limiting the success of pump-and-treat include: (a) aquifer heterogeneity, (b) sorption of the contaminant to aquifer solids, and (c) the presence of a separate immiscible non-aqueous phase liquid (NAPL).

There is a particular need for enhancements to pump-and-treat technology that can overcome the limitations imposed by aquifer heterogeneity, sorption, and the presence of NAPLs. A number of enhanced pump-and-treat technologies have been proposed and demonstrated in the laboratory, but none have been subject to an objective field evaluation, nor is engineering design guidance available for routine application to contaminated ground-water remediation.

The EPA's National Risk Management Research Laboratory (NRMRL), through its subsurface cleanup and mobilization processes (SCAMP) program, and the Armstrong Laboratory, Environics Directorate (AL/EQ) at Tyndall AFB, FL, and both agencies through the SERDP program, have been working on innovative methods to increase the removal rates of toxic organic compounds from the subsurface. This proposal is an enhancement to the programs of both institutions.

7. Project Description:

The objective of this research is to demonstrate processes for enhancing contaminant removal (enhanced pump-and-treat technologies) in a variety of geologic settings and to produce engineering design guidance documents for applying these processes to remediate contaminated ground water. The guidance will address the entire remediation effort, including site characterization and supporting laboratory work, required to achieve the maximum benefit from the remediation technologies included in the study.

The proposed work will be a series of field demonstrations at two or more sites of enhanced pump-and-treat technologies supported by site characterization and laboratory research required to produce a credible field demonstration and a credible evaluation. The work will focus on remediation of sites believed to be contaminated by non-aqueous phase liquids (NAPLs), such as chlorinated solvents. The proposal is to conduct these demonstrations at contaminated DoD sites to increase the likelihood that the results will be directly applicable to actual remediation projects.

The tests will be conducted as small-scale field projects. Each technology will be compared, at the same site, with several alternative remedial technologies including pump-and-treat. The results of these comparisons will show the differential improvement achieved by one process relative to another.

The proposed work will demonstrate and evaluate processes to enhance subsurface contaminant removal that are presently at a stage of development where they can be seriously considered for use in installation/restoration programs at DoD facilities. Such processes include innovative methods, such as: pulsed pumping, to optimize system design and operation for conventional as well as enhanced pump-and-treat; solvent flushing with water-miscible solvents such as ethanol; surfactant flushing; hot water flushing; and methods for forcing fluids through regions of low hydraulic conductivity.

Each evaluation will involve a set of similar tasks: site selection and characterization, design and construction of test facility, operation and monitoring, and evaluation and reporting. Each site will be characterized using state-of-the-art non-invasive and invasive techniques to provide the data necessary to select, design, operate and evaluate the remedial technology under study. Existing research design models will be utilized to develop the actual test facilities. The last part of each demonstration will be an evaluation of the test data and the preparation of a report. The report will describe site characterization, system design and operation, performance evaluation, degree of remediation achieved, cost analysis, factors limiting the success of the technology, and

additional research, if any, required to overcome these limitations. These reports will form the basis for an engineering design guidance manual scheduled for completion 03/99.

The proposed work is a continuation of work performed under SERDP Phase I and Phase III and addresses Thrust 1.H: Solvents Contaminated Groundwater, and Thrust 1.I: Fuels Contaminated Groundwater Pillar 1: Cleanup of the DoD's Tri-Service Strategic Environmental Quality Strategic Plan. The proposed work extends NRMRL's SCAMP research program, which is an effort to improve the efficacy of pump-and-treat remedial actions for ground water contaminated by chlorinated solvents. The proposed work complements the (AL/EQ) Small Business Innovative Research (SBIR) and SERDP (Phase I) funding to encourage businesses to work on DoD environmental problems. A fully contained hazardous waste unit at Hill AFB has been selected as the first demonstration site. The selected site has a mixture of LNAPLs including: POLs, solvents, pesticides, PCBs and Dioxin. A small amount of the LNAPL is still mobile but the majority is now at residual saturation. Hydraulically, the site is sufficiently permeable to permit delivery of the remedial fluid to the point of contamination. The contamination is sufficiently close to the surface to minimize construction cost. State and Federal regulators have been approached to obtain permission to make Hill a demonstration facility for extraction technologies. EPA/RSKERL and AL/EQ both have strong laboratory and field programs directed toward in-situ remediation of contaminated ground water. The subsurface remediation expertise from these programs is available to provide support to the proposed work.

Each of the proposed processes has been shown to overcome some limitations that prevent remediation of contaminated aquifers. However, there are a number factors that have not been field evaluated. Three of these factors are: the high degree of spatial variability in the subsurface environment, the difficulty of obtaining in-situ mixing of a remedial additive with a subsurface contaminant, and changes in the hydraulic properties of the system as the NAPL is removed.

8. Expected Payoff:

Pump-and-treat systems are the primary technology in use at sites with contaminated ground water. Because of their inability to effectively clean up source regions of contaminated waste sites, many of them are being used primarily to provide hydraulic containment; and the forecasts are that they will need to be operated "in perpetuity." The proposed work will allow developing technologies to be implemented faster and with more confidence in their performance. The demonstrations will provide guidance in the application based on carefully documented field experience, which should, in turn, improve acceptance within the regulatory community. Estimated costs for ground-water remediation by DoD and other federal agencies range upwards of hundreds of billions of dollars, and even incremental improvements in efficiency will justify the costs of the proposed research.

9. Milestones/Accomplishments:

1. Select site and technologies for first tests	08/94
2. Initiate site characterization and project design for the first set of tests	08/94

3. Construct and install treatment systems for first set of tests	12/94
4. Initiate first set of tests; collect and analyze operational and monitoring data	12/95
4a. Install remaining test cells at first site	07/95
4b. Initiate within cell characterization in remaining cells at site 1	12/95
4c. Initiate remediation in remaining cells at site 1	03/96
5. Select test sites and technologies for second test	04/96
6. Conduct site characterization and project design for the second set of tests	05/96
6a. Write test report for first tests	05/96
7. Construct and install treatment systems for second test	09/96
8. Initiate second set of tests; collect and analyze operational and monitoring data	03/97
9. Complete data collection for first set of tests and write test reports	05/97
10. Complete data collection for second set of tests and write reports	03/98
11. Produce summary report/engineering design guidance report	03/99

Nine test cells have been installed and instrumented at Operational Unit 1 of Hill AFB, Utah. A reactive tracer technique was developed which permits mapping the level of contamination in three dimensions. The characterization technique has been successfully used in quantifying and integrated contaminate mass both before remediation and after remediation. One of the nine test cells has completed their field activities. In this test cell alcohol was utilized to solubilize the NAPL present. Preliminary analysis of the test results suggest the technique was capable of removing 80% of all contaminants and as much as 100% of some contaminants. The actual remediation took two weeks. To achieve an equivalent level of remediation using pump-and-treat technology would require approximately 2500 years at this site.

10. Transition Plan:

The proposed work will consist of small-scale controlled field demonstrations. The reports and guidance documents resulting from this work will be written such that they will be suitable for full-scale planning and implementation.

The EPA/NRMRL Technology Support Center (TSC) has provided technical assistance on over 300 Superfund sites since 1987. NRMRL has an on-site professional staff with a primary responsibility for technical assistance. NRMRL has conducted numerous technology transfer seminars. The TSC will provide a very effective means for transferring the results of this research to the user community. The Air Force Environmental Systems Program Office (HSC/YAO) and the Air Force Center for Engineering Excellence (AFCEE/ES) will further develop the technical information and finalization of the technical data package. Preliminary principals of practice manuals, technical reports and professional publications will be produced for distribution to appropriate technology transfer offices of the Air Force, Army, Navy, and DOE.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	2,200	2,200	860	1,100	1,300	1,300	2,200	11,160
EPA	530	678	700	750	400	0	0	3058
DoD*	629	462	138	0	0	0	0	1,229
Total	1,659	3,340	1,698	1,850	1,700	1,300	2,200	15,447

* Armstrong Laboratory, Environics Directorate

12. Performers:

The performers for the proposed work are: EPA - National Risk Management Research Laboratory, Ada, OK; University of Florida, Gainesville, FL; MIT, Boston, MA; Rice University, Houston, Tx; University of Oklahoma, Norman, OK; University of Mich, Ann Arbor, MI; Michigan Tech, Houghton, MI; University of Arizona, Tucson, AZ, Clemson, Clemson, SC; CSIRO, Perth, Australia; DoD (Air Force) - Armstrong Laboratory, Environics Directorate, Tyndall Air Force Base, FL; DoD (Air Force) - Environmental Management Directorate, Hill AFB, UT. Cooperative agreements with academic and research organizations already involved in development of aquifer remediation technology will be used to conduct part of the proposed research. CRADAs will be developed as the project progresses.

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14. Keywords:

Extraction, NAPL, Ground-Water, Surfactant, Co-Solvent, Sparging

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Removal and Encapsulation of Heavy Metals from Ground Water/Soil Washing Extract

3. **Agency:** Environmental Protection Agency

4. **Laboratory:** National Risk Management Research Laboratory (NRMRL)

5. **Project ID:** #387

6. **Problem Statement:**

The goals of this proposed applied research (6.2) program are to develop a unique, innovative technological approach for many of the difficult problems, found on DoD facilities: 1) that of removing metal contamination from dilute matrix, ground water process, waste water or soil washing extract: 2) managing metal residuals that can not be destroyed. This effort will (1) develop high-capacity low-cost adsorbents, based on cellulose or starch, natural polymer or synthetic polymers (with functional groups) for selectively adsorbing toxic metals such as lead and copper, and then (2) demonstrate permanent encapsulation of the solid adsorbent matrix by extrusion in recycled plastics such as high density polyethylene for long-term disposal. The metal contaminants (i.e. lead, copper) can be directly adsorbed from ground water or soil washing extract used to treat firing range soil. If present in a solid matrix, the metals can first be leached selectively into a concentrated aqueous medium, which then will be subjected to the low-cost adsorption technique and encapsulation. The proposed research will result in a highly efficient, yet affordable technology for remediating metal contaminated water.

Restoration of metal-contaminated water or solids is a generic problem, at many military sites. Indeed the problem is so extensive that affordable technologies are critically needed now. For ground water or soil washing extract the treatment part usually uses activated carbon or a resin, which on saturation is regenerated by acid leaching. The metals in aqueous stream are then isolated by precipitation. The precipitate sludge is further treated, then disposed of in a hazardous waste landfill. The problem may continue over the years as the metals will gradually form leachates. It has been estimated by industry that for every one dollar of operating cost in the adsorption part of this technology, about 3 to 6 dollars are spent in regeneration. Thus developing low-cost adsorbents that do not need regeneration provides a very attractive technical approach. This is a new idea, no prior art exists.

One dominant method of metals disposal is the cement-based solidification/stabilization process. The long-term effectiveness of this technique, however, has not been determined. Alternatively vitrification has been tried, and proposed especially for radioactive wastes but does not allow for resource recovery of the encapsulated material. Encapsulating metallic wastes in thermoplastics has been demonstrated in the U.S., U.K., France, and Israel, and no leaching has been observed

for a long time (years). Metals and their compounds have no detectable diffusive transport through polymer films. In landfills thermoplastics do not begin to biodegrade in less than 400 years; in low moisture environment and in absence of microbial action, therefore, these encapsulants will last much longer. The thermoplastics are also stable to high levels of irradiation, which is important for storing radioactive compounds. The longevity of these encapsulants of course can be increased by multiple encapsulation. The Brookhaven National laboratory has performed some preliminary work in this area.

7. Project Description:

The project has several distinct parts, requiring different technical skills for their solution. First, low-cost adsorbents need to be designed and developed and produced. In the environmental restoration area, adsorbents such as carbon, zeolites, or ion exchange resins have been used. Each technology is based on the concept of regenerating the adsorbents for reuse. As has been mentioned before, even with regeneration, these adsorption processes tend to be very expensive for large dilute matrices. Moreover these adsorbents do not possess high adsorption capacity (mostly fraction of a percent), which imparts two undesirable effects on process economics, namely adsorbent cost and eventual dilution of the metals on regeneration. Highly selective adsorbents with specific ligands have made chromatography a mainstay in protein separation from very dilute solutions. In that spirit, this effort will develop low-cost adsorbents which have inexpensive but highly efficient ligands attached to them. These adsorbents will have higher capacity and high specificity for chosen metals. The resulting adsorbents will not need to be regenerated.

The technical approach consists of attaching specific amine or imine-based (or other promising) ligands on chosen adsorbents, which can be selected from cellulose, starch, saw dust, peat moss, chitin/chitosan etc., and tested for their efficacy. The engineered material most likely will be in pellets or beads form to maximize fluid flow capacity. EPA will build laboratory apparatus to demonstrate the idea of metals adsorption from contaminated water.

In another section of the project, the separation (volume reduction) data from the laboratory will be used to design experiments for encapsulating the adsorbents.

Important technical issues to overcome: (i) attaching inexpensive ligands to low-cost substrate to impart high capacity, (ii) preparing appropriate engineered (thermoplastic) materials which are easily handled, (iii) demonstrating the stability of the polymers to internal or environmental effects.

8. Expected Payoff:

This technological approach can be tailor-made to many civilian or military site-related problems. For example, contaminated firing range soil are found on many military sites and will be remediated utilizing soil washing technology. This approach will establish a new paradigm in adsorption technology -- i.e. disposal with adsorption without regeneration, resulting in cost savings for DoD site remediation or waste treatment.

Impact: This technology will have far-reaching impact on particularly dilute contaminated matrices for which no inexpensive alternatives exist. Life cycle cost can be reduced if the encapsulating material is recyclable.

9. Milestones/Accomplishments:

1. Develop QAPP (DoD)	05/95
2. Develop QAPP (DOE)	08/95
3. Screen sorbents (DoD)	08/95
4. Evaluate polymer limitations	09/95
5. Select sorbent (DoD)	05/96
6. Produce copolymer (EPA)	06/96
7. Compatibility Evaluation (DoD)	09/96
8. Durability evaluation (DoE)	09/96
9. Demonstration site selection	09/96
10. Develop Demo, H&S, S&A plan	12/96
11. Conduct demo	07/97
12. Demo Report completion at DoD/DOE site	12/97

Sorption work has shown that wood derived products have high capacity and selectivity for lead for a synthetic soil washing extract modelled after the Quantico Base firing range soils. These results indicate that the Army may not need to regenerate ion exchange resins. These sorbents will be loaded at Waterways Experimental Station with actual soil wash extract from Ft. Benjamin Harrison and Picatinny Arsenal. Loaded sorbents will then be sent to Brookhaven National Laboratory for polymeric encapsulation. Final report expected in December, 1996.

10. Transition Plan:

Technical support will be provided to build prototype for demonstration of technology at a DoD.

11. Funding: $(K)

EPA has already allocated approximately $100K towards basic research into low-cost adsorbents research. WES has spent an equal amount on starch xanthates sorption studies.

	FY94	FY95	FY96	TOTAL
SERDP	350	100	500	950

12. Performers:

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14. Keywords:

Adsorbents, Encapsulation, Metal-binding, Firing range, Ground Water

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: Encapsulated Bacteria for In Situ PAH Bioremediation

3. Agency: U.S. Navy

4. Laboratory: Naval Research Laboratory

5. Proposal ID: #23

6. Problem Statement:

This project addresses Requirement 1.I.4.m, and is for the continuation of an existing SERDP-funded project entitled "Encapsulated or Immobilized Enzymes, Bacteria and Nutrients for Remediation of Fuel Spills" and is applied research (6.2/6.3).

The soils and sediments at Naval refueling facilities are often contaminated with petroleum products that are classified as hazardous wastes. The petroleum products that remain as long term contaminants, include polycyclic aromatic hydrocarbons (PAHs; hazardous waste CFR#K001). Removal and cleanup of these materials is expensive and disruptive to Naval operations. Current methods for treatment of contaminated harbor sediments involve dredging with subsequent off-site detoxification. Development of remediation technologies that treat contaminated soils and sediments in situ, would save the Navy considerable expense and eliminate procedures disruptive to Naval operations.

This project addresses the SERDP goals of lowering environmental cleanup costs, compliance with environmental regulations, and unencumbrance of military operations. It focuses on the Thrust Area of cleanup of soil, sediment, groundwater and subsurface water. The overall goal of this project is to develop an in situ treatment strategy using microencapsulated bacteria for low-cost bioremediation of petroleum products that are poorly degraded by naturally-occurring bacteria. In situ treatment strategies lower the cost over ex situ treatments by eliminating the need for expensive excavation, transportation and storage of the hazardous waste prior to detoxification.

If successful, this treatment strategy may be useful for remediation of some toxic hot spots (PAH contamination) in San Diego Bay sediments. The magnitude of the problem, in terms of PAH contamination, is considerable as the sediment of nearly every harbor is contaminated from ship oil and creosote treatment of docks. In San Diego Harbor alone, nearly 4.5 million cubic yards of sediment is being dredged for Naval harbor deepening projects (e.g. carrier turnaround basin, Pier Bravo), with an expected 0.5 million cubic yards being too contaminated for oceanic dumping or beach replenishment projects. According to the San Diego Regional Quality Control Board, once sites in the Bay are declared "toxic hot spots", dredging and off-site disposal will not be legal means of detoxification as a precursor to harbor deepening. In lieu of effective in

situ remediation technologies, such as this microencapsulated bacteria strategy, the Navy will either have to receive an exemption, for the law (which may lead to public relations difficulties) or will have to limit access of Naval vessels to the base. These harbor and pier deepening projects should be considered crucial for continued Naval vessel access to the base. Even if this proposed strategy is not successful at complete removal of the toxicant, treatment may lower PAH levels to the threshold that would allow for the dredging and further off-site cleanup of the sediment.

7. Project Description:

With previous SERDP funding, strains of petroleum-degrading bacteria were microencapsulated in an alginate matrix cross-linked with divalent cation bridges (calcium). The published system has been adapted using an internal set with solid calcium particles. As the calcium slowly solubilizes in the alginate matrix, the cross-linked form which encapsulate the bacteria. This adaptation is expected to reduce ionic stress to the bacteria, resulting in increased encapsulation efficiencies and higher cell viability with long term storage. Higher encapsulation efficiencies and cell viability lowers the cost of the bioremediation treatment strategy.

For the bacterial microencapsulation strategy to be successful and low-cost, the conditions for encapsulation have been optimized to enhance cell viability and petroleum-degrading activity. By developing such a system, fewer microcapsules are needed per volume of treated material, thus lowering the overall treatment cost. Bacterial growth conditions prior to encapsulation have been examined for their effect on cell viability. In addition, the effect of various storage conditions (lyophilization, refrigeration, freezing) on cell viability of encapsulated bacteria was determined to enhance treatment effectiveness. These tasks address the primary environmental concern of ensuring the use of effective and affordable remediation technology.

Microencapsulation of petroleum-degrading bacteria allows for the storage and delivery of strains that are normally found in nature, but may be present in reduced abundance at the spill site. These strains were originally isolated from Superfund sites that were contaminated over decades with creosote. Over time, similar strains will increase in abundance at the spill sites resulting in eventual degradation of the petroleum, but this process may take fifty years or more. The goal is to use microencapsulated bacteria to reduce the contamination level over time scales of months instead of decades. This would reduce exposure of Naval personnel to toxic and carcinogenic waste, and enable the site to be used by either the Navy or the public sector within a reasonable time frame and at an acceptable cost.

Poor performance of in situ treatments involving the addition of bacteria have been due to the unknown effects of site conditions on the ability of bacteria to degrade contaminants. Naval Research Laboratory (NRL) is currently developing specialized indicator strains of bacteria that produce light in response to the presence of bioavailable polycyclic aromatic hydrocarbons (PAH). The indicator strains would enable us to predetermine, whether or not the appropriate nutrient and environmental conditions exist at a site making it amenable to the in situ treatment using microencapsulated bacteria. This system would allow us to alter the site conditions, with nutrients or buffers, prior to adding the bacteria. Though this project involves the construction

of genetically engineered strains for assays, it does not involve the release of genetically engineered bacteria into the environment.

Previously, it has been demonstrated that disturbing contaminated soils has resulted in abiotic removal of the toxin from the site. These treatments have often erroneously been characterized as "bioremediation." To determine whether or not the microencapsulation treatment is resulting in actual bacterial degradation of PAH at the site, newly developed molecular probing techniques (16S rRNA hybridization) will be used to identify the added PAH-degrading bacteria in the soils and sediments. These tasks address the primary environmental concern to implement affordable methods for site characterization, namely the field location and abundance of PAH-degrading bacteria.

The microencapsulated bacteria will be tested as a bioremediation strategy in model microcosm systems (5 liter) and subsequently in pilot-plant scale systems (100 liter). These series of tests will be designed to demonstrate the potential of employing microencapsulated PAH-degrading bacteria, along with essential inorganic nutrients and electron acceptors, as part of an in situ bioremediation strategy. Finally, the system will be field tested in coordination with an EPA project examining the use of stable isotopic methods for determining efficacy of bioremediation treatments. This important collaboration will help determine the effectiveness of microencapsulated bacteria at degrading PAH under field conditions.

8. Expected Payoff:

Using microencapsulated bacteria to detoxify a site of hazardous waste compounds would be a low-cost alternative to excavation and off-site treatment of contaminated soils. Aside from the lower cost of removal of PAH from Naval soils and sediments, an important aspect of the strategy is that Naval operations in the treated areas are less disrupted when compared with treatment requiring excavation and off-site cleanup. It is exceedingly difficult to estimate the dollar value of this savings to the Navy. Also, because of the potential of causing collateral damage to areas adjacent to the treated area, there is sometimes no alternate ex situ treatment that can be used for cost comparison. In situations where soils and sediments are co-contaminated with heavy metals and PAH, removal of PAH allows for the immobilization of the metals with subsequent land filling of the treated materials.

9. Milestones/Accomplishments:

	Scheduled	Completed
1. Development of microcapsule system	11/93	02/94
2. Measure activity of microencapsulated bacteria	12/93	02/94
3. Perform benchtop assays of petroleum degradation	03/94	11/94
4. Determined biosurfactant production important for degradation in encapsulated strains	06/94	10/94
5. Develop storage system for field deployment	06/94	08/95
6. Test treatments in microcosm model systems	06/94	12/94
7. Examine specific attachment system as lower cost alternative to encapsulation for some applications	03/96	

7a. Interim Report (FY94 tasks)	12/95
8. Develop molecular probe techniques for evaluation of treatment efficacy in field test	11/95
9. Transfer immobilized bacteria system to CU030	01/96
10. Develop field assay for prediction of treatment efficacy in field	11/95
11. Transfer field assay to CU030	01/96
12. Initiate field demonstration at PAH-contaminated site in Little Rock Arkansas	01/96
13. First quarterly sampling	03/96
14. Second quarterly sampling	06/96
15. Third quarterly sampling	09/96
16. Final report to SERDP	09/96

The project has succeeded to two thrust areas; microencapsulation technologies; and, molecular genetic strategies for lowering the cost of deploying strains in the field by examining bacterial degradation mechanisms of surface-associated contaminants. Microencapsulation techniques have been developed to increase the viability of bacteria for use in bioreactors or other applications (1 patent application, 1 manuscript). NRL has worked closely with the end users (SBP Technologies Inc.) as well as with US EPA, Gulf Breeze Environmental Research Lab to develop strategies for effective deployment of encapsulated and immobilized bacteria in currently used field remediation strategies (2 conference papers). Technologies developed and evaluated in this project are being transferred for mesocosm and field evaluation in another SERDP-funded project (CU-030; In situ Bioremediation of Fuel and Efficacy Monitoring; POC: CAPT Warren Schultz) over the next two years. Using molecular genetic techniques, NRL determined that the encapsulated strains may be using a biosurfactant for hydrocarbon degradation and may use an attachment mechanism that would allow the adaptation of a groundwater circulation cell for PAH bioremediation (1 conference paper). Along with SBP and EPA, NRL has found these strains to be effective degraders of PAH in a variety of detergent conditions that may be useful for enhancing degradation in the field (1 conference paper).

10. Transition Plan:

The technology will be transitioned to the industrial collaborator, SBP Technologies, Inc. SBP and its parent company, Eicon, have the technology base and expertise and equipment necessary to use this treatment strategy for eventual cleanup of Naval sites. Their research facilities are on-site at the EPA's Gulf Breeze Environmental Research Lab in Pensacola, FL where they work on encapsulated and immobilized cell technologies for creosote degradation in bioreactors.

11. Funding: $(K)

	FY92	FY93	FY94	FY95	FY96	TOTAL
SERDP	180	350	350	0	500	1,380

12. Performers:

The lead organization is NRL Code 6900 (Center for Biomolecular Science and Engineering). The principal contractor is SBP Technologies, Inc. (POC: Dr. James Mueller). Development of methods for determining treatment efficacy is being coordinated with management of an other SERDP funded program. Development methods for determining treatment efficacy is being coordinated with management of a SERDP funded project at EPA (POC: Dr. Raymond Wilhour, Gulf Breeze Environmental Research Lab, Pensacola, FL).

NRL: Dr. Barry J. Spargo, Program Manager, Dr. Michael Montgomery, Environmental Microbiology

Collaboration with Industry: SBP Technologies, Inc., Dr. James Mueller, PAH Bioremediation Ms. Susanne Lantz, Bioremediation.

Collaboration with EPA's Gulf Breeze Environmental Research Lab: Dr. Hap Pritchard, Branch Chief, Bioremediation and Risk Assessment, Dr. Richard Coffin, Microbial Ecology Group Head

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14. Keywords:

Bioremediation; Petroleum; PAH; Bacteria; In situ

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: In Situ Bioremediation of Fuel and Efficacy Monitoring

3. Agency: U.S. Navy

4. Laboratory: U.S. Naval Research Laboratory

5. Project ID: #30

6. Problem Statement:

This project (6.2/6.3) addresses Requirement 1.III.1.g & j. Contamination of soil, sediment and waters by fossil fuel-based contaminants represents the world's largest environmental problem. In the U.S., the frequency of occurrence of fossil fuel contamination is greater in magnitude than that reported for chlorinated solvent pollution. Given the scope and magnitude of these environmental contamination problems, bioremediation often represents the only practical and economically feasible solution. When depth of contamination or nature of the contaminated material precludes all other remedial actions short of the no-response alternative, in situ treatments are frequently recommended. However, cost-efficient and effective implementation strategies need to be specifically developed and/or refined to address these needs, At the same time, unequivocal approaches for demonstrating in situ bioremediation of target contaminants need to be established.

With past support of the SERDP program we have developed and refined innovative in situ bioremediation strategies, including approaches using stable carbon and nitrogen isotope geochemistry to monitor progress during in situ bioremediation of polycyclic aromatic hydrocarbon (PAHs) and other priority pollutants (e.g., BTEX). Approaches in stable isotope geochemistry may allow one to monitor progress of the bioremediation effort by tracing the fate of individual compounds of interest, including bacterial assimilation and respiration, formation of toxic intermediates, and transport of the compound from the site. With this information, a mass balance for the contaminant may be conducted and efficacy of various bioremediation approaches may be tested.

To establish tests using stable isotopes as a monitoring protocol for bioremediation, SERDP has funded researchers at Gulf Breeze Environmental Research Laboratory (GB-ERL), Texas A&M University (TAMU), Naval Research Laboratory (NRL) and SBP Technologies, Inc. (SBP) to setup stable isotope laboratories and to conduct preliminary experiments. The objective of the current proposal is to transition this 6.2/6.3 research, through a series of field demonstration programs, yielding valid, cost-efficient technologies for in situ bioremediation and on-line performance monitoring.

7. Project Description:

Collaborating researchers at GB-ERL, TAMU, NRL, and SBP received funds in June 1993. The progress of the collaborations to date is as follows. Two laboratories have been equipped with elemental analyzer/gas chromatograph/isotope ratio mass spectrometers (EA/GC/IRMS). One system at TAMU is dedicated to measuring natural abundance stable isotopes. The other system at GB-ERL is set up for experiments with tracer additions of stable isotopes. Each is equipped so that carbon, nitrogen and sulfur isotope ratios may be measured as gasses, gross organic matter or as individual compounds. One is also equipped with an ion trap mass spectrophotometer (GC/IRMS/ITMS) to assist with compound identification. This addition will make it possible to follow intermediate compounds during the degradation process.

The development of methods to measure bioremediation effectiveness involved the in situ degradation of PAH mixtures in laboratory systems. Drs. Cifuentes and Coffin have measured the natural abundance carbon isotope ratio of CO_2 that is evolved upon degradation of various mixtures of compounds. Results indicate a direct correlation between the stable isotope ratio of CO_2 respired and the carbon source consumed by the bacteria. This information suggests that on-line monitoring of CO_2 carbon isotope ratios will be appropriate for examining, monitoring, and evaluating the bioremediation of contaminant mixtures.

Along with the development of stable isotopes monitoring tools, SBP has integrated innovative technologies and support from various industrial collaborators (i.e. Beazer East, Inc., Chevron, Corp., IEG Technologies, Inc.) to yield large scale practical applications for in situ bioremediation strategies. Various modifications of in situ soil flushing, aeration and groundwater circulation technologies have proven effective for simultaneous treatment of vadose/phreatic zone soil, capillary fringe, groundwater and saturated soil contaminated with refined petroleum products at over 100 sites world-wide. However, successful application to environments contaminated with more biologically persistent compounds, such as jet fuel constituents and certain PAHs, has been somewhat limited. Presently, there are few examples of successful in situ bioremediation projects in the technological database. Moreover, trial demonstrations of more conventional bioremediation approaches, such as hydrogen peroxide injection and pump-and-treat technologies have met with limited success in their applications to PAH contaminated environments. Two key factors responsible for the poor performance are low bioavailability of contaminant and low abundance of PAH-degrading microoganisms.

The program objective is to demonstrate the usefulness of innovative in situ bioremediation technologies by introducing inoculants and maintaining their activity in the field. The project approach is to develop the treatment strategy, identify the contaminated site, employ the biotreatment in small scale laboratory tests, and finally in a large-scale field demonstration. This project has three unique thrust areas: development of techniques for measuring effectiveness of bioremediation treatments; integration of multiple technologies for treatment strategy; and, use of bacterial encapsulation and inoculation for enhancement of PAH degradation in the field. Laboratory studies will model the biodegradation on individual chemicals by axenic bacterial cultures available in our culture collections. The studies will be used to measure biodegradation rates, identify catabolic intermediates, assess the formation of toxic end-products, and perform

mass balance of the contaminant under controlled and defined conditions. Similar studies will be conducted with field samples to define the fate and effect of parent compounds and biotransformation products for mass balances.

Samples of contaminated soil will be thoroughly characterized according to standard methods. Contaminants will be extracted, fractionated and chemically analyzed. The natural abundance isotope ratios of these materials will be determined. These values will be compared with those for indigenous carbon sources (i.e. humic materials, humin, fulvic acid, etc.) Knowing these values, mineralization of contaminates will be assessed by the $^{13}C/^{12}C$ ratio of liberated CO_2. These values will be compared with those generated using more conventional chemical and biological analyses. The effect of various amendments on contaminant degradation by naturally-occurring bacteria will be determined.

A mesocosm will be constructed to conduct studies examining the ability of in situ soil flushing and groundwater circulation well (GCW) technology, combined with subsurface bioreactors employing co-immobilized biodegradation agents to biodegrade PAHs. The mesocosm will be loaded with aquifer material artificially contaminated with a known amount of pollutant. The system will be monitored using on-line measurements of microbial respiration, water movement, etc. Stable isotope analyses will be used to monitor the fate of transformed chemicals. This test system will allow for the mass balance chemical analysis to document biodegradation of target compounds using stable isotope techniques. As recommended by the SERDP Science Advisory Board (SAB), field-scale demonstrations will be conducted at contaminated sites to test the efficacy of the monitoring technology across different remediation strategies. Sites will be offered through collaboration with Beazer East, Inc. and the National Hydrocarbon Test Site. Sites will be characterized and the bioremediation process will be monitored for 2 years. Field work will be conducted to use natural abundance stable isotope to measure degradation of PAH and BTEX contaminants. This work will involve surveys of natural abundance isotope ratios of pollutant compounds, extracted mixtures of pollutants, indigenous/natural organic matter, contaminant organic matter and CO_2 evolving from field sites.

8. Expected Payoff:

Techniques for assessing efficacy of remedial technologies are critically needed. Such tools are essential to help ensure that the efforts undertaken are effective and that the remedial technologies are implemented in a cost-efficient manner. Using conventional chemical and biological assays in combination with the proposed on-line stable isotope analyses developed here, offers an ability to follow assimilation, respiration, immobilization, transport and biotransformation of pollutants in situ. The payoff is development of the first unequivocal assessment of treatment efficacy for in situ bioremediation strategies.

9. Milestones/Accomplishments:

	Sched.	Resched.	Comp.
FY 96 Milestones (Project year 3)			
Program start	10/94		
Port Hueneme GCW and Biocurtain			
4th sampling event	12/95		
5th sampling event	03/96		
6th sampling event	07/96		
Reporting	10/96		
Port Hueneme Biopile #1			
4th gas sampling	06/95	10/95	
terminate	07/95	11/95	
Reporting	01/96		
Port Hueneme Biopile #2			
time-zero sampling	09/95		09/95
1st gas sampling	10/95		
2nd gas sampling	11/95		
3rd gas sampling	12/95		
4th gas sampling	01/96		
Reporting	03/96		
Gainesville			
initiate dye test	09/95	10/95	
2nd quarter sampling	08/95	09/95	09/95
inoculate bioreactor	09/95	10/95	
system maintenance	09/95		09/95
3rd quarter sampling	11/95		
system maintenance	11/95		
4th quarter sampling	02/96		
system maintenance	02/96		
Report on dye study	04/96		
5th quarter sampling	05/96		
system maintenance	05/96		
6th quarter sampling	08/96		
system maintenance	08/96		
Reporting	10/96		
Mesocosm			
exper. #1 a/b	03/95	10/95	
exper. #2 a/b	06/95	12/95	
exper. #3	08/95	02/96	
exper. #4	10/95	04/96	
report	12/95	06/96	

An *in-situ* bioremediation systems based upon geological data from boring logs was designed and installed at the NEX, Pt. Hueneme, and Cabot/Kopper's Superfund site, Gainesville, FL. All monitoring and sampling equipment were installed and operational at both Pt Hueneme, CA and Gainesville, FL. A GC-IRMS method for PAH's was developed that permits resolution of major PAH's and provides 0.2% precision. Good chromatographic separation of CO_2 and CH_4 was achieved with a Carboxen 1006 Plot column. Precisions achieved with 400 ng injections of CO_2 and CH_4 were 0.3%. Existing extraction protocols for humic material from soils were tested in the laboratory and found to be as efficient as those reported in the literature. Large quantities of humic acids were extracted from soil for use in biometer flask experiments. Stable carbon isotope ratios were used to assess degradation of fluoranthene by bacterium EPA505. Field samples are being assessed for measuring assimilation, respiration, immobilization, transport and biotransformation of pollutants *in situ.*

10. Transition Plan:

Rapid and successful transition of developed technology from demonstration stage to full scale implementation is enhanced through the active participation of SBP Technologies, Inc. and other industrial affiliates (IEG Technologies, Inc.). SBP is a wholly-owned subsidiary of The EICON Group, Inc. (EICON), which employs 150 professionals in myriad areas of environmental science. EICON is the umbrella company for SBP, Florida Groundwater Services, Inc, (FGS), Florida Remedial Services, nc. (FRS), Westcott & Mapes, Inc. and EICON Surveys, Inc. Out of 9 offices nationwide. SBP offers environmental biotechnology and remediation services with sister companies's providing more conventional engineering and architectural services. With a number of dedicated end-users (i.e. Beazer East, Inc, Chevron) active in this and previous stages of technology development, we are convinced that we have integrated expertise in all aspects of technology development, commercialization and full-scale implementation of systems.

11. Funding: $(K):

	FY94	FY95	FY96	Total
SERDP	2,455	850	700	4,005

12. Performers:

The lead organization is U.S. Naval Research Laboratory, Code 6115, Environmental Quality Sciences Section (POC: Dr. Barry J. Spargo)

EPA National Health and Environmental Effects Laboratory- Gulf Breeze, FL (POC: Dr. Richard B. Coffin)

Texas A&M University (POC: Dr. Luis A. Cifuentes)

SBP Technologies, Inc. (POC: Dr. James G. Mueller)

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14. Keywords:

Bioremediation, Petroleum, PAH, Bacteria, In situ

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Air Sparging and In-Situ Bioremediation Research and Demonstration

3. **Agency:** U.S. Army

4. **Laboratory:** Picatinny Arsenal, New Jersey

5. **Project ID:** #744

6. **Problem Statement:**

Goal: Bioremediation enhancement to air sparging technology may provide a cost effective strategy for removing trichlorethylene (TCE) and related chlorinated solvents from ground water. However, unresolved technical issues focus on quantifying the incremental benefit and designing efforts to stimulate microbial degradation. The overall goal of Phase I of this project is to develop laboratory and field methods for determining the effect of sparge gas-composition on the partition of mass removal due to volatilization and microbial processes. The methods will be demonstrated at Picatinny Arsenal, New Jersey, a site with a well-characterized plume of TCE contamination. Phase II of the project will involve the design and operation of a full-scale sparging/bioremediation demonstration at Picatinny Arsenal based on the findings of Phase I. The overall project will resolve technical and institutional issues that inhibit operational use of the technology.

Background: Air-sparging and coupled in-situ bioremediation has been implemented at the Savannah River site. The Savannah River Project was designed as a scientific demonstration. In addition, the site is characterized by specific geochemical conditions, most notably, the plume was aerobic. An anaerobic contaminant plume, like the one at Picatinny Arsenal, is perhaps more typical of TCE plumes, and introduces questions related to the rate of adaption of the microbial consortium and engineering considerations related to induced precipitates.

TCE is the dominant contaminant in a plume within an unconfined glacial aquifer at Picatinny Arsenal. The unconfined aquifer is about 50 feet thick in the vicinity of the contaminant plume. In 1991, the highest measured concentration of TCE was 21,000 micrograms per liter. In 1986, the site was selected by the USGS Toxic Substances Hydrology Program as its research site chlorinated solvents. Research includes characterization of TCE, related contaminants, and contaminant geochemistry in the aquifer and the unsaturated zone, and fate and transport evaluation. The Army has initiated an interim action under CERCLA to contain and treat the plume by pumping before it enters a continuing source of contamination may necessitate that the pump and treat operation continue indefinitely. The enhanced sparging technology could mitigate this condition.

7. Project Description:

Technical Objective: The objective is to develop methods to quantify the total rate of removal of TCE contaminant for an air sparging remediation system adapted to enhance contaminant removal with aerobic cometabolism. The total rate of removal is the sum of a component due to physical stripping (volatilization) and a component due to aerobic cometabolism. Both components will be quantified to allow for an evaluation of the cost effectiveness of the microbial enhancement. The methods are to be demonstrated at an existing site of TCE contamination and in the laboratory with porous media collected from the site.

Technical Approach: The workplan has three major components: (1) development of methods to conduct sparging/cometabolism laboratory experiments with contaminated sediment, (2) application of overall method to pilot scale experiments at Picatinny Arsenal, and (3) development of a mathematical model to analyze the transport of sparged vapor phase constituents from the water table to extraction wells for the purpose of determining the distribution of mass flux across the water table.

Site geochemistry will be monitored to assess initial conditions with respect to a wide range of inorganic and organic solutes. Initial site assessment will also include analysis of sediment cores to define lithology, total contaminant mass, physical characteristics, and selected microbial guild characterizations.

Laboratory experiments will be conducted with sediment collected during the site assessment described above. Two types of experiments will be conducted: closed systems microcosm experiments and open system column experiments. The microcosm experiments will determine the feasibility of aerobic cometabolism over the range of anticipated geochemical conditions and methane concentration. The open column experiments will allow for emulation of the field experiments under controlled conditions. Cores of sediment taken from the Picatinny site will be instrumented for the columns. Control experiments conducted with pure nitrogen as the sparge gas will provide physical removal rate information to be compared with experiments conducted with sparge gases with various methane and oxygen concentration. These experiments will allow for quantification of the effect of varying design parameters on system performance. The information obtained for the Picatinny sediment will allow for the rational design of pilot-scale experiments.

Pilot scale sparging experiments will be conducted at Picatinny Arsenal within the well-characterized site. The purpose of these experiments is to apply the overall method in-situ and to demonstrate the scaling up of laboratory information and application of the mathematical model (discussed below). The experiments will be conducted with a single sparge well. Mass removal rates will be calculated by collecting vapors with a vapor extraction well and analyzing the exhaust stream for a wide suite of vapors, including TCE and related contaminants, methane as well as signature gasses like carbon dioxide, oxygen, and hydrogen sulfide. The monitoring will allow for separation of removal into a physical volatilization component and into a microbial component inferred by stoichiometric relationship to signature gases. It is anticipated that the experiment can be repeated at the same location to study variable injection rates and methane

loading after a time interval passes which allows for the recontamination of the sparged column from surrounding ground water. It is anticipated that pilot scale experiments can be by-passed in subsequent operational applications of the technology.

A mathematical model of the vapor extraction process will be constructed to determine the spatial effect of the sparge well by allowing for the calculation of constituent-specific mass flux across the water table to the extraction well. Reactions that occur in the unsaturated zone while TCE, methane and oxygen are in transit to the extraction well(s) will also be simulated. This model is currently under development at USGS. It will be completed, applied, and published as a public domain code during this project.

8. Expected Payoffs:

(1) Development of methods for performance evaluation and development of design criteria for air sparging with bioremediation enhancement.

(2) Demonstration of methods at a site with geochemical conditions different than previously investigated at Savannah River.

9. Milestones/Accomplishments:

1. Project start	02/94
2. Finalize work plan, finish literature search	05/94
3. Begin instrumenting site. Site assessment	05/94
4. Begin laboratory microcosm experiments	07/94
5. Begin air-permeability tests	09/94
6. Complete air-permeability tests	12/94
7. Finish site assessment/instrumentation	02/95
8. Begin field air sparging experiments	04/95
9. Begin field cometabolism experiments	05/95
10. Start laboratory column experiments	03/95
11. Complete laboratory microcosm experiments	07/95
12. Finish laboratory column experiments	08/96
13. Complete field cometabolism experiments	11/96
14. Final report	12/96

Preliminary stoichiometric relationships for the cometabolic biodegradation process have been developed using the microcosm data. This relationship is currently being tested in the flow-through column experiments and will be used to evaluate the effectiveness of the microbial enhancement in the field experiments. The development of the air-flow model and methods of analyzing air-flow pathways in the field will assist in evaluating other sites for such remediation.

10. Transition Plan:

The subject technology, which was develop under a DOE program, will be implemented at a DoD site under regulatory auspices of the U.S. Environmental Protection Agency and the New Jersey Department of Environmental Protection and Energy. Appropriate aspects of the project will be published in peer review journals.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	557	271	321	1,149

12. Performers:

U.S. Army - Coordinate contractor procurement and regulatory compliance

U.S. Geological Survey - responsible for conducting Phase I research

Private Contractor - assist in the design of vapor extraction system and development of unsaturated zone transport model in cooperation with U.S.G.S.

Hazardous Substance Management Research Center (HSMRC) - coordinate and chair expert advisory panel which will provide technical oversight

Expert Advisory Panel:

Dr. Richard Brown - Groundwater Technologies Inc., Princeton, N.J.
Dr. Peter Jaffe - Dept. of Civil Engineering, Princeton University
Dr. Peter Lederman - Director, Center for Environmental Engineering and Science, N.J. Institute of Technology
Dr. Brian Looney - Westinghouse Savannah River, Aiken, S.C.
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14. Keywords:

Air Sparging, TCE, Chlorinated Solvents, Bioremediation Enhancement, Ground Water Remediation

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Explosives Conjugation Products in Remediation Matrices

3. **Agency:** U.S. Army Corps of Engineers

4. **Laboratory:** USAE Waterways Experiment Station (WES)

5. **Project ID:** #715

6. **Problem Statement:**

During investigations of potential treatment technologies for explosives contaminated soils, specifically during bioslurry treatability studies and composting, TNT has been observed to interact with some component of the treatment matrix in such a way as to preclude extraction with organic solvents. Similar interactions have been observed in explosives amended soils. Mass balance determinations using radiolabelled TNT reveal that the radioactivity is still present in the matrix in some unknown form. As much as 80 percent of the radioactivity added to tests is accounted for in the unextractable matrix. Therefore, the parent compound has not been completely destroyed, but has changed to a more complex form. The long-term stability and environmental safety of these uncharacterized conjugates are unknown. Objectives of this basic research include characterization of these explosives conjugates, development of an analytical methods for identifying them in treatment systems and in soils, and determining the long-term stability and environmental safety of the conjugates. Accomplishment of these objectives will ensure the development of effective remediation technologies that ameliorate environmental health effects and lead to a more complete characterization of the end products of new treatment technologies. Research was initiated to determine the basic mechanisms of interactions between TNT and humus, soil enzymes and clays under SERDP in FY 93. This proposed research would expand upon that effort.

7. **Project Description:**

The project will consist of five tasks as follow:

Task 1: Characterization of interactions of explosives with humus and other organic components of soils and remediation matrices.

Task 2: Characterization of interactions of explosives with clays and other mineral components of soils and remediation matrices.

Task 3: Development of an analytical method for identifying conjugates in various matrices.

Task 4: Determination of the role of microbiological processes in formation and stability of conjugates.

Task 5: Assessment of the ecotoxicology of conjugates.

The ability of explosives to form conjugates with soil organic fractions (i.e., humin, humic acids, fulvic acids, and enzymes such as peroxidase, laccase, and tyrosinase), clays (i.e., montmorillonites and kaolinites), and other mineral components of remediation matrices (i.e., oxy/hydroxy compounds of iron and other minerals) will be evaluated. The influence of environmental factors such as temperature, Ph and moisture regimes on development and characteristics of conjugates will also be determined. Classical extraction and analytical techniques have been ineffective in removing and describing these unextractable conjugates. Therefore, innovative analytical techniques such as surface plasmon resonance, microcalorimetric titration, and new application of high performance liquid chromatography, X-ray diffraction and nuclear magnetic resonance will be applied. The role of microbial processes in the formation of the conjugates through precursor compounds or conjugation of explosive to microbial cell walls will be investigated. Factors affecting stability of the conjugates to leaching and microbial degradation will be determined.

Characterization of the ecotoxicology of conjugates answer the question of whether conjugates in soils and remediation matrices are environmentally compatible. An appropriate bioassay/biomarker suite will be selected based on the chemical nature of the parent compounds, the conjugates, and the potential functional groups present in metabolites. The potential for reappearance of toxicity from hydrolysis and re-release of parent compound or from the formation of toxic metabolites will be investigated. Microbial mutagenic and cultured cell line *in vitro* assays, and whole organism adult and early life-stage bioassays will be used. The influence of environmental factors on bioavailability and on the time course of toxic potency will be determined.

Specific user requirements that will benefit from performance of this work include:
(1.I.1.b) Technology for removal of energetics/other organics contamination (A,N)
(1.I.4.c) Decontamination of soils containing energetic materials (A,N,AF)

8. Expected Payoff:

This study will improve existing and future remediation technologies by identifying the composition and potential environmental impacts of explosives conjugates. The credibility of several existing technologies will be enhanced with regulatory agencies and with other users who are concerned with the ultimate safety and environmental effects of explosives. An understanding of the nature and properties of conjugation products formed during remediation and their fate and effects may also lead to new approaches to remediation.

9. Milestones/Accomplishments:

1. Evaluate dialysis methods for assessing interaction with soil organic
2. Select bioassay/biomarker toxicity tests for determining environmental safety
   of conjugates (WES) 03/95
   components (Natick) 03/95
3. Evaluate extraction and/or derivitization techniques for analytical methods
   development (CRREL) 07/95

4. Evaluate hydrolysis procedures for release of intact contaminants (CRREL)	09/95
5. Evaluate surface plasmon resonance for measuring binding kinetics of organic conjugates (Natick)	12/95
6. Determine degradation rates for soil fractions containing explosives conjugates (WES)	07/96
7. Characterize products of microbial degradation (WES)	07/96
8. Determine enzymatic degradation of soil fractions containing explosives conjugates (WES)	09/96
9. Develop extraction and analysis procedures (CRREL)	09/96
10. Interim Report	10/96
11. Determine microbial mutagenicity and conduct *in vitro* assays (WES)	09/97
12. Determine conjugation kinetics (Natick)	09/97
13. Determine precision and accuracy of analytical method in various matrices (CRREL)	06/97
14. Conduct whole organism and early life stages bioassays (WES)	09/97
15. Identify factors controlling biodegradation of conjugates (WES)	09/98
16. Characterize organic conjugates from natural soils (Natick)	09/98
17. Determine ruggedness of analytical method (CRREL)	09/98
18. Determine effects of environmental factors on toxicity (WES)	09/98

For milestone 3, two enzymes, a phenoyloxidase and horseradish peroxidase were tested. Evaluation of hydrolysis procedures for this milestone indicated that mild acid hydrolysis caused the release of TNT transformation products, but not the parent compound. Milestone 4 was completed with the determination that surface plasmon resonance was not a good tool for evaluating binding kinetics for explosive conjugates because interaction between the ligands (explosives) and the dextran matrix were inefficient.

10. Transition Plan:

Those who are developing remediation technologies will have access to results and their implications for 6.2 and 6.3a levels as they are developed through conference presentations and published reports. Direct interactions between principal investigators of this project and other relevant projects under Environmental Quality and Technology Program 6.2 remediation technology work units and SERDP work units will be initiated in the form of briefings and informal discussions.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	500	496	200	300	500	1,996

12. Performers:

The lead laboratory for the proposed research is the U. S. Army Engineer Waterways Experiment Station who will be responsible for completion of Tasks II, IV and V. The U. S. Army Natick Research, Development, and Engineering Center will conduct Task I and contribute to Task II. The U. S. Army Cold Regions Research and Engineering Laboratory will conduct Task III. At least one cooperative agreement with a university is anticipated.

13. Principal Investigators:

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14. Keywords:

Explosives, Conjugates, Remediation, Analytical Methods, Toxicology, Microbiology

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Integrated Biotreatment Research Program: From Flask to Field

3. **Agency:** US Army

4. **Laboratory:** USAE Waterways Experiment Station (WES)

5. **Project ID:** #720

6. **Problem Statement:**

The DoD has literally thousands of sites that are contaminated with organic compounds that pose a serious threat to the environment on land entrusted by the public to be properly maintained by the DoD. As part of the realization by DoD of its responsibility toward cleanup of the numerous sites contaminated from past military activities, the majority of these sites are slated for cleanup (remediation). Unfortunately, the remediation of these sites using existing technologies is problematic from an economic, technical, and political point of view. Current technologies for soil and groundwater are incineration and phase change technologies (activated carbon and air stripping), respectively. The projected costs associated with site restoration using these current technologies are astronomical. All too often because of these high costs, landfilling is selected instead of true on-site remediation. From a technical point of view, phase change technologies do not result in the on-site destruction of the contaminants posing serious disposal and transportational problems. Politically, siting of an incinerator is a publicity nightmare. Also, the US Environmental Protection Agency (USEPA) and DoD is encouraging strong investment and application of innovative technologies. Of all the innovative technologies under development and in some cases, application, biotechnologies are considered by most remediation experts to be the most promising.

Biotreatment processes have been successfully demonstrated for treatment of a variety of contaminants. Research, regulatory, and user communities collectively agree that biotreatment of easy-to-degrade compounds, such as fuels and simple phenols, are established processes. Based on the success of these biotreatment applications, a strong potential exists for development of biotreatment processes with expanded application toward more difficult to degrade contaminant groups such as explosives, chlorinated solvents, polychlorinated biphenyls (PCBs), and carcinogenic (heavy) polycyclicaromatic hydrocarbons (cPAHs). Several governmental and academic research groups are currently investigating biotreatment techniques for treatment of these traditionally difficult to degrade contaminants. Although a high potential exists for development of vastly improved remediation techniques using biological processes for remediation of media contaminated with these compounds; unfortunately, sporadic and often sparse funding and inaccessibility to actual sites have severely hindered process development. Other factors contributing to the delay of process development include poor intercommunication

between research groups, the lack of design and application engineering input into research plans, and poor technology transfer to applied research and technology user groups.

This program is proposed as a 6.2/6.3 program that will enhance, but not duplicate, existing funded efforts in the DoD STRAT Plan. This program also fits nicely into USEPA's long-term research plans. The following DoD user requirements will be met or partially met by performance of this R&D program:

Treatment system for water contaminated with organic contaminants.
Improved fate, effects, and transport models for groundwaters.
Treatment system for water contaminated with chlorinated and defense hydrocarbons.
Treatment of Navy relevant contaminants in salt/brackish/groundwater matrices.
Isolation and treatment technology for contaminated surface water impoundments.
Treatment system for water contaminated with mixtures of chlorinated solvents.
Process to remediate groundwater contaminated with hydrocarbon fuels.
Decontamination of soils containing energetics materials.
Contamination under buildings and roads.
Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
Technologies for isolation and decontamination of sludges.
Dredged soil area decontamination and reclamation.
Improved marine sediment remediation technologies for metals, organics, and PCBs.
Improved shore and open Ocean hazardous materials cleanup/restoration.
Enzyme and bacterial treatment technology.
Decontamination of soils containing energetic materials.
Improved cleanup procedures at locations where UST leaked.

7. Project Description:

This project represents a collective research initiative by several key governmental and academic organizations with a long history of developing treatment technologies. All of the partnering organizations are bringing into the initiative not only experience, but additional funding and experimental resources that will be "dovetailed" into this comprehensive program. The partnering approach proposed will ensure that appropriate scientific and engineering disciplines interact to form a formidable research team of a magnitude never attempted within the DoD environmental biotreatment research program. The project will be approached through investigation of several primary technical issues. The level of research effort expended on each issue will vary depending on state of the art for that issue. The ultimate goal of this program is to perform research efforts that will result in the fielding of several biotreatment processes for remediation of predominant DoD contaminants.

The proposed experimental approach will be to first investigate a variety of promising biotreatment techniques at the bench scale. During performance of bench activities, engineers with design and implementation experience (the Baltimore COE District) will assess the overall implementation potential and projected costs associated with these techniques. This effort will

ensure that the research groups are developing processes that are realistic and on firm technical ground. Upon completion of the bench efforts several small scale pilot studies (referred herein as intermediate scale) will be performed using those techniques considered most promising. After performance of the intermediate scale studies, at least four of the most economically and technically sound processes will be evaluated on the field pilot scale at actual DoD sites.

The primary technical issues to be addressed in this research initiative are listed and briefly discussed below:

Issue I. Biotreatment of Explosives Contaminated Soils and Groundwaters. A variety of promising biotreatment techniques will be investigated for remediation of soil and groundwater contaminated with explosives compounds. Explosives contamination represents one of the most prevalent organic contamination within the DoD. Although research into the feasibility of biotreatment of explosives has been undertaken by both DoD and USEPA over the last few years, funding limitations and the lack of a comprehensive research approach have hindered significant advances toward the field scale. The following biotreatment mechanisms will be investigated for explosives:

a. Enzymatic degradation performed under a variety of controlled systems. Controlled enzyme manufacturing methods will also be investigated.
b. The use of specialty surfactants, both manufactured and natural, will be evaluated for their ability to enhance the bioavailability of the explosives compounds to the microbial populations during treatment.
c. The metabolic pathways and biodegradation of key intermediates.
d. Alternating redox conditions and techniques for establishment of either condition within an active bioreactor system.
e. The use of genetically altered microorganisms as reactor seeds.
f. Use of plants to treat contaminated groundwaters.
g. Evaluate pre-and post-biotreatment oxidation techniques for complimenting biotreatment approaches.

Issue II. Soils and Groundwaters Contaminated with Chlorinated Solvents. Chlorinated solvents represent a class of contaminants that is detected at more DoD sites (and CERCLA and RCRA sites for that matter) than any other contaminant group. Several significant breakthroughs in the biological degradation of these compounds have been made over the last several years; however, limited funding and access to contaminated sites has hindered further development. Issues under investigation for chlorinated solvents within this program include:

a. Bioventing of chlorinated solvents using aliphatic oxygenase pathways via addition of simple aliphatic gases (i.e. propane, methane, etc.).
b. Evaluation and modeling of enzyme production and substrate interactions.
c. Anaerobic biodegradation in aqueous and soil phase systems.
d. Develop design oriented Biokinetic Models.
e. Bioslurry treatment using process air recirculation.

Issue III. Soils and Sediments Contaminated with PCBs. Soils and sediments contaminated with PCBs represent one of the most challenging compound groups under investigation in this project; yet, development of a viable biotreatment process could result in significant savings to the DoD. PCBs are found at many DoD installations due to improper disposal of hydraulic fluids and waste lubricating oils. Primary issues under investigation are:

a. Degradation and production kinetics of enzyme based degradation.
b. Cycling of redox conditions from anaerobic to aerobic as a means of dechlorinating higher substituted Aroclors into lower substituted, easier to degrade Aroclors.
c. Use of surfactants both natural and manufactured as a means of enhancing bioavailibity during biological treatment.
d. An evaluation of candidate cometabolites for enhanced degradation of selected PCB Aroclors.
e. Use of genetically altered microorganisms as potential seed sources.
f. Evaluation of various natural isolates and consortia toward PCB biodegradation using a variety of biotreatment systems.

Issue IV. Soils Contaminated with cPAHs. This group of contaminants represent the most regulated of PAH compounds due to their carcinogenic properties. Also, because of their large and complex molecular structure, they also represent the most difficult of all the PAHs to biologically degrade. Key research issues are:

a. Surfactant, both natural and manufactured, for enhancing biodegradation rate in a variety of biotreatment systems.
b. Evaluation of candidate cometabolites for initiating and economically maintaining effective cPAH biodegradation rate.
c. Use of genetically altered organisms for enhancing biodegradation.
d. Cascading aerobic bioslurry treatment.
e. Composting techniques for degradation of highly complex cPAH contaminated matrices.
f. Evaluation of various natural isolates and consortia activity toward cPAHs under a variety of implementation scenarios.

Issue V. Development and Design of Specialty Reactors. Many of the biological systems required for implementation of concepts under development in this project require specialty reactors. Periodically, the results of the various contaminant specific activities will be reviewed for determination and selection of appropriate implementational strategy and respective reactor type. As expected, the actual reactor designs will be governed by the breakthroughs and conditions dictated by the results of the above listed study issues. Expected reactor designs that are to be developed are:

a. Zero-head aerobic bioreactors which utilize hydrogen peroxide as and/or gas permeable membranes alternative oxygen sources.
b. Evaluation of solid and semi-solid oxygen sources for both *in situ* and *ex situ* strategies.
c. Cascading bioslurry systems (as mentioned above in the cPAHs section).

d. Improved process gas recirculation systems for treatment of contaminated media containing volatile compounds such as chlorinated solvents.
e. Reactor systems for treatment of refractory compounds and low level contaminated groundwaters.
f. Evaluation of low carbon loaded attached growth systems for treatment of low level contaminated groundwaters.
g. Development of biocells as an economically attractive reactor option.

Issue VI. Applications Potential of Genetically Engineered Microorganisms. Although science is rapidly approaching the time when genetically altered organisms may play an important part in future bioremediation processes; unfortunately, the political and social implications surrounding these organisms may hinder implementation of these organisms into reactors. This project will assess and identify problems associated with implementation of engineered organisms. A logical plan of action in terms what actions may be taken to accelerate and enhance the use of these microorganisms will be drafted.

Issue VII. Toxicity Reduction. The success of treatment will be assessed on processes selected for intermediate scale evaluation using a variety of toxicological assays used to properly quantify toxicity reductions.

8. Expected Payoff:

The primary benefit of this study is reduced remediation costs associated with development of "realistic" biotreatment processes for cleanup of contaminated DoD sites. Projected treatment costs are expected to fall at or below the \$150 per cubic yard of soil treated (incineration costs are usually above \$350/cy) or \$.50 per thousand gallons of groundwater treated (carbon costs are usually greater than \$1.00/Kgal). Secondary benefits include; expanded implementation potential of existing and developing biotreatment processes, biotreatment technologies that result in the on-site destruction of contaminants, increased regulatory and political acceptance of DoD cleanup activities will be realized as these technologies are used, and increased user acceptance of the technologies will be realized because of the involvement of the user community (COE-Baltimore District) within the project structure.

9. Milestones/Accomplishments:

Major milestones for this program are listed below. For each milestone listed at least a WES report will be drafted by the performing research group; however, each partner involved in the milestone will be encouraged to publish the report under their agency framework to accelerate transfer of information to the user community. The primary, completion based milestones (assuming a two year FY funding life) are:

1.	Biocell field pilot scale study	12/95
2.	Complete field scale phytoremediation	09/96
2.	Low level organic loaded bioreactor field pilot study	06/96
3.	Field pilot scale evaluation of zero-head bioreactor	09/96

4. PAH bench scale studies	09/96
5. Report on fielding potential of engineered microbes	09/97
6. Chlorinated solvent bench studies	09/98
7. PAH intermediate scale study	09/98
8. Explosives bench studies	09/98
9. Chlorinated solvents intermediate scale studies	09/98
10. PAH field pilot study	09/99
11. PCB bench scale studies	09/99
12. Explosives intermediate scale studies	09/00
13. PCB intermediate scale studies	09/00
14. Explosives field pilot scale studies	09/00
15. PCB field scale study	09/00

Completed shake-flask experiments on both TNT and RDX mineralization. This experiments indicates that RDX can be mineralized up to approximately 50% under both aerobic and anaerobic conditions. This finding is very exciting since we are the first group to report significant mineralization under aerobic conditions. Also, the extent of anaerobic mineralization is by far the highest reported. The TNT results were not as encouraging. We did get excellent removal; however, none of the systems indicated double-digit mineralization within the soil slurries. All known by-products were removed, but still significant mineralization was not observed.

Phytoremediation experiments are proceeding nicely. TNT is rapidly removed; however, RDX is still problematic via its persistence. This issue is a problem that we must solve if phytoremediation of explosives is going to be feasible.

Culturing of isolates active toward chlorinated solvents is proceeding nicely. Characteristics of appropriate organisms are being defined which will greatly enhance our capability to apply anaerobic techniques in the field.

We have completed the first biocell pilot study at Port Hueneme. The results are very encouraging. We plan to perform a second pilot effort this February.

EFX Inc., in conjunction with CERL and USAF-Tyndall is working with us to evaluate the low-carbon loaded system. The system was transported to EFX in December and activities have begun.

10. Transition Plan:

The results of this study will be presented in a form that will easily be utilizable by AEC, COE, USEPA, and the private sector for demonstration and implementation. Efforts will be made to collaborate with private organizations for enhanced process development through CRADAs. Additional collaboration with the USEPA via the SITE program will also be investigated. Also,

partnering efforts with AEC, DoD installations, and USEPA/COE will be encouraged as an additional means of technology transition.

In addition to official project reports, partners within this program will be encouraged to publish in peer reviewed journals, present information at national and international symposia, and informal briefings at DoD, COE, and USEPA offices. Additional tech transfer will be encouraged through an annual open symposia at WES where the results from this program and related partnering activities will presented by the various program partners. One final note, the efforts proposed in this program directly fit in the DoD Tri-Services STRAT plan.

11. Funding: $(K)

The funding requirements for this program and collective partnering 6.2 research funds and reimbursable funds:

	FY94	FY95	FY96	FY97	FY98	FY99	FY00	TOTAL
SERDP (6.2)	2,450	1,101	1,962	2,150	2,400	2,250	3,000	15,313
USA	1,500	1,250	800	1,000	500	0	0	5,050
USAF	500	500	100	0	0	0	0	1,100
USN	500	300	300	0	0	0	0	1,100
USEPA	1,500	1,500	500	100	100	0	0	3,700
DOE	500	500	500	500	500	0	0	2,500
GLRC	300	300	200	200	0	0	0	1,000
TOTAL	6,250	5,451	4,362	3,950	3,500	2,250	3,000	29,763

12. Performers:

The partners for this research initiative are listed below. Under each partnering agency, at least one point of contact is presented.

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14. Keywords:

Biotreatment, Explosives, Polychlorinated Biphenyls, Chlorinated Solvents, Polycyclicaromatic Hydrocarbons, Bioreactors

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Surfactant-Enhanced Biodegradation of Contaminants

3. **Agency:** U.S. Army

4. **Laboratory:** USAE Waterways Experiment Station

5. **Project ID:** #731

6. **Problem Statement:**

Overall Goal: This research will investigate the basic processes limiting the bioavailability of contaminants sorbed to soils and evaluate the applicability of biologically-mediated, desorption-enhancing processes to increase microbial destruction of these contaminants.

Problem Statement: The DOD has over 12,000 sites contaminated with a variety of energetic and organic compounds. Long-term persistence of these materials in soils is directly related to poor mobility of the contaminants and to resistance of the contaminant to microbial degradation. Many of these organic contaminants are sorbed onto clays or organic matter in soils. Through a combination of sorption processes, the contaminant may move deep into soil pores and/or clay mineral lattice structures, effectively immobilizing the contaminant. Inability of sorbed contaminants to partition back into the aqueous phase severely limits microbial degradation of contaminants in soil treatment systems. Correspondingly, effective biotreatement for those compounds is impaired because the bacterial are unable to contact the sorbed compound. As a result of these processes, immobilization is a significant problem to overcome in site restoration.

Current remediation technologies are deficient. Incineration is expensive and bioremediation often fails. Mobilization of contaminants is highly desirable for the development of new remediation technologies and improvement of existing technologies. For example, initial research at the U.S. Army Engineer Waterways Experiment Station (WES), the U.S. Environmental Protection Agency Athens Environmental Laboratory (AERL), and the U.S. Naval Surface Weapons Center (NSWC) indicates that certain surfacants can accelerate microbial degradation of TNT and chlorinated aromatic hydrocarbons and the microorganisms produce bioemulsifiers that may promote removal of contaminants previously bound to the soil. Other investigators indicate that enzymes modify certain contaminants that strongly sorb to soil, altering their affinity for soil by modifying the structure of substituents on the contaminant molecule. As a result, an intermediate transformation product having increased solubility may be produced, thus enhancing complete microbial degradation of the contaminant.

Enhancing the effectiveness of bioremediation will require an integrated investigation of the physical, chemical and biological factors affecting sorption of organic contaminants as they relate to bioavailability. The information gained from the 6.1 level basic research can be directly applied to 6.2 level investigations to promote bioremediation technologies.

Project Objectives: Determine the role of sorption on availability of contaminants to microbial degradation. Reduce costs for microbial treatment of soils in sites contaminated with explosives and other organics by identifying ability of microbially-supported, desorption-enhancing processes to overcome sorption limitations.

Status of Project: Research was initiated to identify basic sorption processes and determine their possible relationship to microbial degradation of contaminants under SERDP in FY 93. This proposed basic research will further develop that effort in conduction with preliminary work supported under the Environmental Quality and Technology Program. This research is jointly submitted by the US Army (WES) and the US Navy (Naval Surface Warfare Center) and US EPA (ERL-Athens) for SERDP funding.

7. Project Description:

Technical Objectives: Determine the significance of soil sorption on biological availability of representative explosives, Chlorinated pesticides, polychlorinated biphenyls (PCB's) and polycyclic aromatic hydrocarbons (PAH's). Provide procedures to determine the most effective means by which microorganisms overcome sorption limitations. Develop methods to determine applicability of microbiologically-mediated, desorption-enhancing processes to improve microbial destruction of contaminants. Provide this information in a form suitable for use at the 6.2 level.

Technical Approach: Determine the importance of sorption in controlling bioavailability of several organic contaminants of military importance and identify the means microorganisms utilize to overcome these limitations. This will be accomplished in a series of tasks listed below. Critical portions of Tasks II, III, and IV require application of several microbiological and biochemical technologies that are at the cutting edge of present-day research. For this reason, the proposed research could not have been undertaken 2-3 years ago.

a. Task I. Compare diffusion of organic contaminants within soil particles with microbial degradation to determine limiting rates and focus research on the more significant knowledge gaps. Identify suitable systems in which to study processes. Determine presence or absence of biosurfactant and/or bioemulsifier production by key microbial species active in contaminant degradation.

b. Task II. Develop techniques for investigating sorption sites on and diffusion within soil particles. Develop techniques for investigating movement of microorganisms producing biosurfacants and/or bioemulsifiers processes having sorption-modifying capabilities.

c. Task III. Develop predictive sorption kinetics models to evaluate importance of sorption to bioavailability and select the most appropriate procedures for determining sorption

limitations. Develop a data base for verification of general predictive techniques with soils having a wide range of properties.

(1) Procedures for determining impacts of sorption on microbial availability, including equipment, chemicals, and methods.
(2) Guidance on how to interpret results.
(3) Guidance for application of predictive techniques. Descriptions of procedures to evaluate ability of microbial processes to overcome sorption limitations.
(4) Develop technology transfer documents, seminars and laboratory demonstrations to transition the technology to 6.2 level. Where appropriate, supply technology in a form suitable for direct application to 6.3 level.

Relationship to DoD/EPA Environmental Objectives: Information obtained from the performance of this study will contribute to several DoD/EPA environmental remediation objectives. This work will improve contaminant destruction technology by enhancing bioavailability of contaminants sorbed to soil. Specific user requirements that will benefit from performance of this work include:

(1.I.4.c) Decontamination of soils containing energetic materials (A,N,AF)

(1,I.2.i) Contamination under building and roads (A,N,AF)

(1.I.4.n) Remedial treatment technology for soils contaminated with chlorinated and nonchlorinated organics (A,N,AF).

(1.I.1.g.) Treatment systems for water contaminated with Chlorinated and dense hydrocarbons.

(1.I.3.a.) Technologies for the isolation and decontamination of sludge.

(1.I.2.e.) Improved marine sediment remediation technologies for metals, organics and PCBs.

(1.I.4.c.) Decontamination of soils contaminated with energetic materials.

(1.I.1.j) Treatment of Navy relevant contaminants in salt/brackish/groundwater matrices.

(1.I.1.e.) Processes to remediate groundwater contaminated with hydrocarbon fuels.

(1.I.1.n.) Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.

(1.I.2.b.) Dredged sediments area decontamination and reclamation.

(1.I.6.c.) Isolation and treatment technology for contaminated surface water impoundments.

(1.I.2.i) Contamination under building and roads.

(1.I.6.d.) Improved shore and open ocean hazardous material cleanup/restoration.

(2.III.1.d) Enzyme and bacterial treatment technology.

(2.III.2.d) Improved cleanup procedures at locations where UST have leaked.

8. Expected Payoff:

Potential Users: DoD, DOE, private Superfund, and Resource Conservation and Recovery Act (RCRA) site managers will benefit from procedures to enhance bioremediation. Development of this technology will allow cost-effective in-situ and landfarming biotreatment of soils and sediments contaminated with explosives and other organic compounds. Current soil incineration techniques destroy local ecosystems. The technology will also benefit ex-situ techniques, such as bioslurry reactor treatment. This will be especially important at those sites where microbial destruction of crystalline TNT is required.

Positive impacts: This study will integrate technology development and basic research to provide better means to develop the most cost-effective treatment options. Rapid determination of factors affecting microbial accessibility to contaminants has the potential to decrease the overall costs of in-situ, landfarming and bioslurry treatment of contaminated soils.

9. Milestones/Accomplishments:

Major milestones under this work effort are listed below, along with the respective month and year they will be completed.

$234K	FY95 Milestones:	Planned
1.	Rate the most promising biosurfacants/microorganisms	5/95
2.	Produce biosurfacant in sufficient quantities to be evaluated ex situ.	11/95
3.	Investigate structure-function relationships of ex-situ added biosurfacants and bioemulsifiers with contaminated soils.	12/95
4.	Evaluate in situ survival and performance of best surfactant-producing microorganisms in sorbents and soils (Task II)	12/95

$379 K FY96 Milestones:	Planned
1. Select the best performing biosurfacant - contaminant system for bench-scale study (Task II)	10/95
2. Optimize performance of the selected biosurfacant - contaminant biotreatability system at bench scale.	
3. Develop and verify predictive desorption and microbial degradation models (Task III)	4/96
4. Research Progress Meeting	6/96
5. Derive treatment cost data for biosurfacant enhanced degradation.	8/96
6. Develop protocol to enhance microbial accessibility (Task IV)	

Pending Funding FY97 + Milestones:	Planned
1. Examine abilities of microorganisms to produce surfacants and emulsifiers in microcosms (Task IV)	1/97
2. Verify predictive techniques for desorption enhancement in selected soils (Task III)	3/97
3. Research Progress Meeting	3/97
4. Develop protocols for enhancing microbial accessibility (Task IV)	5/97
5. Document predictive models for sorption (Task III)	6/97
6. Write guidance for desorption enhancement (Task V) 16 Conduct technology transfer seminars and workshops (Task V)	7/97

Seven strains of bacteria which produced bioemulsifiers active against PCB and PNAs sorbed to soils. Two of the microorganisms, Pseudomonas sp. Y4 and Burkholdaria cepacia ENV391 can also metabolize all but the most highly chlorinated PCB congeners via the 2,3,- and 3,4-dioxygenase pathways. The anionic glucose lipid emulsifier produced by these microorganisms and lichensysen produced have been shown to be at least 10 times more effective than synthetic surfactants at solubilizing hydrocarbons in soil - water systems. Degradative gel electrophoresis has shown soils contaminated with PAH contained a DNA band that was unique to Pseudomonas putida. This indicates that some members of the Pseudomonades which produce bioemulsifiers and degrade contaminants may survive and function in contaminated soils. Nucleic acid banding patterns (i.e., finger prints) are being determined on the other perfomant strains so that their survival in various soils can be assessed. Studies designed to assess the cost effectiveness of using synthetic surfactants, biosurfactants purified from a fermenter and biosurfactant produced in situ have been under way at Port Hueneme since November.

10. Transition Plan:

This 6.1 level research will directly support bench-scale assessments at the 6.2 level. As work progresses, briefings and direct input by principal investigator will be provided to relevant Environmental Quality and Technology Program 6.2 level biotreatment work units and corresponding work units in the environmental programs of other agencies. In addition, the proposed work will directly support the work developed in the Integrated Biotreatment Research Program SERDP proposal developed by WES. Technical assistance for these purposes will be available during and after the course of the research. The technology will also be transferred through technical papers, presentations, and work unit reports. Professors, post-doctorals and graduate students will be involved in helping to develop the studies and conduct the work, which will indirectly aid education. We will also consider application of this technology to suitable field scale technologies through use of cooperative research and development agreements (CRADAs).

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	700	234	397	1,331

12. Performers:

The lead laboratory for the proposed research will be the U.S. Army Engineer Waterways Experiment Station (WES). WES will make contributions to all the tasks and have responsibility for Tasks II, IV, and V. The NSWC Biotechnology Laboratory, Silver Springs, MD will have responsibility for Task I and will make major contributions to Tasks II and III, plus some contribution to Task V. MSU will make some contributions to Task I, major contributions to Tasks II-V and have primary responsibility for Task III. The NSWC will continue cooperative work with the University of Maryland; MSU will conduct some research on desorption kinetics and biodegradation with competitive cooperative agreements. WES will work with either the Hazardous Substance Research Center/South and Southwest or the Hazardous Substances Research Center/West. WES may also work with Texas A&M in it University Research Initiative with the Army Research Office. WES personnel will interact directly with university personnel through the Visiting Professor Program, with the National Research Council Doctoral Program, and by direct contacts between WES and graduate students.

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14. Keywords:

Mineralization, Sorptive Processes, Bioavailability, Surfactant, Reduction.

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: National Environmental Technology Test Sites Program (NETTS) Army National Test Locations for Explosives and Heavy Metals, Volunteer Army Ammunition Plant (VAAP), Chattanooga, TN and Louisiana Army Ammunition Plant (LAAP), Shreveport, LA

3. Agency: U.S. Army

4. Laboratory: Army Environmental Center

5. Project ID: #723

6. Problem Statement:

The current process for gaining acceptance of cost-effective, innovative environmental technologies for the remediation of federal installations is laborious and costly. The problem stems from several causes which have the cumulative effect of hampering innovation, impeding technology transfer, and hindering accelerated cleanup. Analysis of the technology development and transfer process has shown that these problems exist because of the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures which meet requirements of regulators and users, and the lack of information disseminated in formats suitable for all interested parties. The first problem mentioned above can only be addressed through collective technology analysis implemented through diverse agency review and administration. The latter causes can be addressed by a comprehensive technology, demonstration, evaluation, and transfer program. The NETTS provides such a technology demonstration, evaluation, and transfer program. The NETTS provides test locations for comparative demonstration and evaluation of cost-effective and innovative environmental technologies which will enable transfer from research to full-scale use. The Departments of Army, Navy, Air Force, and EPA are partners in NETTS, and there six test locations. These goals are being accomplished through the following initiatives: (1) involvement of users, regulators, and the public throughout the course of technology demonstrations; (2) providing test locations, infrastructure, and field support required for the demonstration and evaluation of innovative technologies under comparable and well-characterized climatic and hydrogeologic conditions; (3) standardization of data collection and analysis protocols among the partnering DoD Services and EPA; (4) querying regulators, users, and the public to ascertain what information resulting from technology demonstrations should be collected, reported, and the presentation format preferred to facilitate understanding and acceptance of the technology's performance capabilities; (5) providing test beds for supporting environmental research; and (6) proactive commercialization through widespread dissemination of technical evaluations, guidance specifications, and cost and performance data. Each NETTS test locations has been developed to provide well-characterized test sites and the infrastructure required for technology demonstration. By providing dedicated and focused sites National Test Locations allow better

use of resources and prevent duplication of effort because the selection, permitting, characterization, infrastructure, and on-site field support are already in place for each new technology demonstration in contrast to one-off, developer-staged demonstrations. In addition to infrastructure, field support, and demonstration oversight, the Army with the assistance of the other NTL managers, developed a comprehensive technology demonstration guidance document. This document includes guidance and/or boiler plates for writing test plans, criteria and guidance on collecting and reporting cost and performance data , QA/QC plans, technology demonstration execution success criteria, regulatory and user interface, and technology transfer strategy. The guidelines document is a common link among the tri-Services and EPA to expedite the development of innovative and more efficient cleanup technologies. A cost-and-performance database which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed under the McClellan AFB NETTS project. EPA provides additional programmatic guidance and support to each NETTS test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

7. Project Description:

The contamination of soil, sediments, and groundwater by explosives and heavy metals has become a problem at many DoD industrial facilities due to past disposal practices. Under the auspices of NETTS NTLs have been established which focus on solving military unique priority contaminant situations and concerns. The Army's objective in this program is to expedite the development, demonstration, and transfer of effective environmental technologies aimed at characterizing, remediating or attenuating sites contaminated with explosives and heavy metals. To satisfy the need for providing NTLs, the Army has selected and developed both Volunteer Army Ammunition Plant (VAAP) and Louisiana Army Ammunition Plant (LAAP) for technology demonstration and evaluation of environmental technologies which may be effective at characterizing, remediating or attenuating sites contaminated with explosives and heavy metals. The Army selected two locations as NTLs for technology demonstration due to differing hydrogeologic conditions and varying spectrums of heavy metals and of explosives contamination at the respective sites which should allow extrapolation of a successfully demonstrated technologies' performance standards to other sites with similar contamination across the nation. At VAAP, soil and ground water contaminants consist principally of explosives and explosives manufacturing-related contaminants (TNT, DNT, and nitroaromatics), with some heavy metals (Cr, Cu, Pb, As, Be, Co, and Ni) present in a few areas of the installation. Most soil contamination is located near old buildings, or their remains, that were used to batch-manufacture TNT. Contamination has been detected in the vadose zone but has not been traced to entry points. Conversely, at LAAP which was placed on the National Priorities List in October 1984 due to ground water contamination from Area P Lagoons, investigations have shown that the upper aquifer is contaminated with explosives possibly resulting from receiving explosives contaminated wastewater (pinkwater) from various manufacturing operations during the 1940's. An RI/FS identified six other areas of concern at LAAP, five of which include: two burning grounds, a landfill, an electroplating waste lagoon, and a chromium etching facility. Soils and ground water are contaminated with metals (Ti, Pb, As, and Cr), explosives (TNT, DNT, tetryl, RDX, HMX, and various related nitroaromatic compounds), and solvents. In addition, the VAAP NTL location offers an on-site laboratory, which can be utilized by both NTLs, that has the

capabilities for providing immediate analytical feedback on technology demonstration process parameters, as well as associated QA/AC. There will also be a technology selection committee of explosives or heavy metal experts (depending upon the contamination) to identify the technologies for demonstration. The criteria will include the maturity of the technology applicability to DoD needs, potential to meet established clean up levels, and potential cost savings over currently used technologies. Selected technologies can come from governments laboratories, or from private firms under Broad Agency Announcement solicitations or through Cooperative Research and Development Agreements.

8. Expected Payoff:

Immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) return on investment and cost savings for SERDP sponsored and other technology demonstrators; and (6) advanced understanding of the fate and transport of contaminants. In addition, by including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each NETTS test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate long-term payoff will be lower remediation costs for the federal government.

9. Milestones/Accomplishments:

A. General

A.1.	HPLC data review and database input	07/95
A.2.	Model for graphical site characterization	07/95
A.3.	Site characterization data input to IRDMIS	08/95
A.4.	Developed List of Tech Review Committee	08/95
A.5.	EPS Treatability Study	08/95
A.6.	TLM WBS developed	09/95
A.7.	Prepared brief to SAB, TTAWG, and SERDP	09/95
A.8.	Tech Demo Cost Data for Value Added Analysis	10/95
A.9.	Final NETTS Guidelines document	12/95

B. VAAP

B.1.	SCAPS demonstration	05/95
B.2.	Site orientation training procedures developed	09/95
B.3.	Review of Sun River tech demo proposal	10/95

B.4.	Review of EPS prelim tech demo proposal	10/95
B.5.	Coord w/ state for contaminant transport	11/95
B.6.	Notification to state regarding waste streams	11/95
B.7.	Submission of lab validation packages	12/95
B.8.	Explosives manufactures workshop	12/95
B.9.	Partnering agreement w/EPS	12/95
B.10.	GW pumping for Tech Demo	12/95
B.11.	On-site OSHA training	01/96
B.12.	EPA Region IV Lab Phyto Bench Scale	01/95
B.13	EPS Advanced Oxidation Demo	02/96
B.14.	WES Peroxone system	03/96
B.15.	EPA Eco Monitoring Res Div Biomarker	04/96
B.16.	WES Phyto pilot study	05/96
B.17.	USAEC/WES SCAPS	06/96
B.18.	WES fluidized bed aerobic reactor	07/96
B.19.	ERM Thermophilic Aerobic Treatment	TBD
B.20.	Sun River Advanced Oxidation	TBD

C. LAAP

C.1.	Provide on-site laboratory (canceled)	11/95
C.2.	Complete Draft LAAP EA	01/96
C.3.	Complete Draft LAAP Health & Safety Plan	01/96
C.4.	Complete LAAP site characterization	02/96
C.5.	Complete site preparation	03/96
C.6.	Sevenson chrome remediation	TBD
C.7.	WES Natural Attenuation Study	TBD
C.8.	WES GW transport TNT modeling	TBD

In FY94 the Army screened several candidate facilities and installations involved in the Army's Defense Environmental Restoration Program (DERP) for the purpose of selecting a suitable explosives NTL. By the end of FY94 the USAEC had negotiated and coordinated with the appropriate parties for the establishment of VAAP as the Army's NTL for explosives.

During FY95 the Army performed administrative, logistical, and management functions necessary to establish VAAP as a NTL. These activities included: conducting site and environmental assessments; NEPA documentation; permit and regulatory review; development of site specific management, QA/QC, and health and safety plans; test site infrastructure development; on-site laboratory set-up and validation; and coordination with potential government, industry, and academic technology demonstrators. Concurrent with these efforts the Army performed its first technology demonstrations at VAAP and developed LAAP as a satellite Army NTL due to its differing hydrogeologic conditions, heavy metals contamination, and broader spectrum of explosives contamination. In addition, the Army managed the development of the NETTS Guidelines for Quality Technology Demonstrations document which will assist the tri-services

and EPA NETTS partners in the effort to execute uniform technology demonstrations and implement common analytical protocols.

10. Transition Plan:

Cost and performance data will be collected by the standardized methodology and entered into the NETTS cost-and-performance database being developed by the Air Force NETTS PI. At the conclusion of each demonstration each respective technology demonstration project PI will write a technology evaluation report and produce a technical data package. From these, the TLM will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the TLM, which will provide regulators, users, and the public with the information, presented in a useable format, necessary to obtain technology acceptance and expedite transfer to commercial use. Other technology transfer efforts will include technical short courses, seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration brochures and videotapes.

11. Funding: $(K)

	FY 93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
Test Location/Mgmnt/ infrastructure	2,180	1,110	350	500	750	750	750	6,390
QMP Development	830	210	0	0	0	0	0	1,040
TOTAL SERDP	3,010	1,320	350	500	750	750	750	7,340

12. Performers:

Overall policy administration and program guidance is provided by the SERDP Program Office for NETTS. Specific project management and oversight of the Army's portion of the SERDP NETTS is performed by the U.S. Army Environmental Center. Additional project support has been procured by the USAEC from Tennessee Valley Authority (TVA) whose expertise and geographical proximity to the NTLs allows greater project monitoring, coordination, and on-site presence. Each Army NTL is located on government owned/contractor operated (GOCO) facilities. On-site technology demonstration support is performed by the facilities' operating contractors who are ICI Americas, Inc. and Thiokol Corporation for VAAP and LAAP, respectively. Development of the NETTS Guidelines for Quality Technology Demonstrations document was managed by the USAEC TLM and performed by TRW, a private contractor that also conducts background site characterization when needed. For purposes of coordination within the NETTS, each National TLM is a member of a TLMs' committee, which comprises

SERDP representatives as well as the respective tri-service and EPA TLMs. This committee represents a Tri-Services and EPA coordinated effort focused on partnering with other organizations to adopt uniform reporting formats and implement uniform test protocol guidance.

13. Principal Investigator:

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14. Keywords:

Energetics, Explosives, Heavy Metals, National Test Location, Technology Demonstration, Demonstration Site

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: National Environmental Technology Test Sites Program (NETTS) Navy National Test Location for Fuel Hydrocarbons, Naval Construction Battalion Center (NCBC), Port Hueneme, CA

3. Agency: U.S. Navy

4. Laboratory: Naval Facilities Engineering Service Center (NFESC)

5. Project ID: #863

6. Problem Statement:

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The National Environmental Technology Test Sites Program (NETTS) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in NETTS.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each NETTS test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-time, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each NETTS test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding (Army Environmental Center lead), the NETTS is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed (Armstrong Laboratory, Tyndall AFB). EPA provides additional guidance and support to each NETTS test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

7. Project Description:

The objective is to support NETTS and to demonstrate systems for characterizing and remediating soil, sediments, and ground water contaminated with fuel hydrocarbons and/or waste oil.

The NCBC Port Hueneme National Test Location management will provide NETTS programmatic, infrastructure and technical support for fuel hydrocarbon and waste oil characterization and remediation demonstrations. NETTS support will include development and integration of the following: (1) QA/QC procedures, (2) test protocol guidance, (3) demonstration reporting format, and (4) cost and performance data retrieval guidance.

Infrastructure at NCBC Port Hueneme and its management (operation and maintenance) will include: (1) monitoring wells, (2) in-line sensor network, (3) ex situ treatment facility with hazardous material handling capability, (4) utilities, and (5) contaminated soil, sediments and ground water resources. Technical support to demonstration project PIs will include: (1) characterizing and monitoring contaminants, (2) processing permits, (3) supporting stakeholder involvement, and (4) transferring technologies.

8. Expected Payoff:

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each NETTS test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other

Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government and wide spread use in the environmental characterization and cleanup industry.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for characterization and cleanup; (2) establishment of a research and development platform for

advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

The NCBC Port Hueneme National Test Location for fuel hydrocarbon and waste oil provides the following: (1) well characterized test sites, (2) controlled field conditions for comparative evaluations of technologies, (3) uniform evaluation criteria for demonstrations, reporting of results and technology transfer, and (4) cost savings through amortization of infrastructure and management.

9. Milestones/Accomplishments:

Test Location Management

1. Contracts awards to GSA for infrastructure O&M	07/95
2. Contract award to MCA Engineering for sensor network O&M	07/95
3. Contract award to Geo-Insight contaminant historical database	07/95
4. Forward 2nd quarter monitoring reports	07/95
5. Forward 3rd quarter monitoring reports	10/95
6. Operate and maintain NTL Infrastructure (on-going)	12/95
7. Support NETTS (on-going)	12/95
8. Conduct quarterly Fuel Hydrocarbon Advisory Committee meetings (on-going)	12/95
9. Participate in community relation forums (on-going)	12/95
10. Support technology transfer (on-going)	12/95

Demonstration Oversight

1. Conduct SCAPS LIF demonstration (729-A)	4/95
2. Complete Biopile (phase I) demonstration (020-N)	7/95
3. Start HAVE demonstration (020-N)	8/95
4. Start Biopile (phase II) demonstration (020-N)	9/95
5. Biocell (phase I) (720-A)	11/95

Supported three SERDP projects including their required permitting and infrastructure. Supported the Oxnard Plain Military Community Public Relations Process. Completed two SERDP project demonstrations. Four SERDP projects are in the process of completing their Application Analysis Reports following a format found in the Quality Management Plan.

10. Transition Plan:

Cost and performance data will be collected by the standardized methodology and entered into the NETTS cost-and-performance database (when available, McClellan AFB lead). At the conclusion of each demonstration, the PI for the demonstration project will write a technology

evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	800	650	900	600	750	750	750	5,200

12. Performers:

The NCBC Port Hueneme National Test Location for fuel hydrocarbon and waste oil characterization and remediation demonstrations is managed from within the Installation Restoration Division of the Naval Facilities Engineering Service Center (NFESC). The commanding officer of the Naval Construction Battalion Center, Port Hueneme is the steward of the base and is ultimately responsible for the results of remedial actions which takes place on the base where the NTL is located. The CBC environmental officer represents the CBC command concerning oversight of the NTL and his staff supports the obtaining and retaining of permits. Contractor support is used to operate and maintain (O&M) the NTL infrastructure at Port Hueneme.

For purposes of coordination within the NETTS, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

13. Principal Investigator:

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14. Keywords:

National Test Location, Fuel, Solvent, Fuel Hydrocarbon, Waste Oil, Remediation, Technology Demonstration, Demonstration Site

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: National Environmental Technology Test Sites Program (NETTS) Air Force National Test Location for DNAPLs, Groundwater Remediation Field Laboratory, Dover AFB, DE

3. Agency: U.S. Air Force

4. Laboratory: Armstrong Laboratory, Environics Directorate, (AL/EQ)

5. Project ID: #866

6. Problem Statement:

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The National Environmental Technology Test Sites Program (NETTS) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in NETTS, and there are six test locations. Each NETTS test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

The goal of the SERDP NETTS is to enable efficient demonstration of candidate innovative technologies for detection, monitoring and cleanup either on an individual basis or in parallel with similar technologies, under representative hydrogeological and climate regimes as found at many contaminated sites in the DoD. The NETTS will provide test beds for research to fully understand the mechanisms in proposed treatment processes. Test beds will be fully characterized and monitored areas where new technologies can be quickly and effectively demonstrated. This will save time and money for technology demonstrators and SERDP by providing on-site management, precharacterization, and more timely permitting.

Dense, nonaqueous phase liquids (DNAPL) contamination poses one of the most challenging problems facing the Department of Defense (DoD) in its attempt to comply with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). DNAPL is a term used to describe a number of materials which are immiscible with, and denser than, water. As a result of these properties, they migrate downward when spilled on the ground, and can migrate below the water table. Especially once below the water table, they are difficult to locate and remove. For the Air Force, the term DNAPL is virtually synonymous with chlorinated solvents, used for years as industrial cleaners and degreasers and responsible for the contamination at approximately one third of all Air Force contaminated sites. Currently there are no acceptable methods for removing or treating the bulk of solvent material that inks into aquifers or is trapped within the soil interstices. These technologies must be developed to protect the public for any health risks associated with DNAPLs which are found in the subsurface at a large number of Air Force bases as well as hundreds of other public and private contaminated waste sites.

7. Project Description:

The Groundwater Remediation Field Laboratory (GRFL) is the Armstrong Laboratory, Environics Directorate (AL/EQ), contribution to the NETTS. Its primary focus is the provision of a Contained Release facility to research and demonstrate technologies for detection, monitoring, and cleanup of DNAPLs. On-site NETTS management and regulatory interface established for the GRFL also support technology development efforts to be demonstrated elsewhere at Dover AFB at existing, well-characterized contamination sites.

The project's goal was to construct and operate the GRFL at Dover, AFB, DE. Construction and operation activities consist of detailed characterization, installation of test cells and monitoring wells, and provision of a temporary building and fencing. Operations consist of emplacement of the constituent (primarily TCE), demonstration of innovative technologies, and disposal of associated wastes.

Test cells will be spaced approximately 50 feet apart. They are constructed and operated in a way to minimize the potential for environmental contamination. Basic design consists of interconnected, steel barrier piling sections (2 feet width) forming a rectangular cell. Test cells will range from 36 to 1800 square feet. The sheet piling is specifically manufactured to allow for joining of one sheet pile to another. The joints will be tremie-sealed with bentonite grout to ensure a tight seal. By driving the sheet piling 3-5 feet into the underlying clay aquitard (approximately 30-40 feet below the surface), a coffer is formed which prevents vertical and lateral migration outside the confines of the box. Additionally, a secondary containment coffer will be constructed surrounding the primary coffer, and is similarly sealed at the bottom and at each joint. The annulus between the cell is filled with water to produce an inward hydraulic gradient. The annulus and inner cell is continuously monitored for leakage. Both upgradient and downgradient monitoring wells, which are designed to also function as an emergency pump and treat system if required, are installed outside the secondary coffer. A vapor barrier is installed to retain solvent within the experimental universe, both to achieve mass balance and to prevent air emissions.

Risks for the project as designed are well controlled. The primary risk is that material introduced into a cell might escape and contaminate an aquifer. Vertical migration is retarded very well by a twenty foot thick clay layer with a hydraulic conductivity four orders of magnitude less than the overlaying strata. Double sheet piling, grouting, monitoring, the emergency pump-and-treat system, and distance to the nearest potential receptors virtually eliminate any risk from lateral migration. A worst-case risk analysis has shown that risk of significant aquifer and surface water contamination and human health impact is negligible even in the unlikely catastrophic event that one barrier is eliminated, the remaining one is seriously ruptured, no emergency treatment is attempted, and the TCE source area is left in place indefinitely.

8. Expected Payoff:

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each NETTS test location provides opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

There are many contaminated sites where field experiments, which provide excellent opportunities to verify some of the conclusions drawn from laboratory experiments, are being performed. However, a number of gross assumptions must be made since these experiments are being conducted in previously contaminated aquifers. These assumptions include, but are not limited to: the amount and composition of the contamination originally introduced into the soil/water matrix, the exact location where the contamination was introduced, and the initial condition of the soil/water matrix prior to contamination. To eliminate the need to make these assumptions, it will be necessary to monitor the development of contaminant plumes from their inception, while maintaining a strict mass balance of the contaminants. This information can be obtained only from well-planned, carefully-controlled experiments involving contained releases of DNAPL materials into naturally deposited soil.

For this purpose, AL/EQ, Tyndall AFB, FL is establishing the GRFL. It will be a unique resource for the Cleanup community by providing opportunities for development of technologies for cleanup of DNAPL materials. The primary purpose of the GRFL will be to provide contained release cells for DNAPL contamination research and development.

9. Milestones/Accomplishments:

A. Test Location Management	
1. Contained Release Site Preparation (including site characterization) begins	08/95
2. Site Preparation complete	02/96
3. Laboratory Emplacement completed	02/96
4. First Contained Release cell constructed	01/96
5. Safety plan completed	01/96

B. Demonstration Oversight

1. Support Enhanced Anaerobic Biodegradation of Chlorinated Organics (RTDF)	01/95
2. Support SCAPS tunable laser demonstration (729-A)	04/95
3. Support SERDp Pulsed-Pumping Demonstration	01/95
4. Support AATDF: Co-oxidation of TCE/JP-4 during Bioventing	01/96
5. Support RTDF Natural Attenuation Study	TBD/96
6. Support SERDP Funnel-and-Gate Demonstration (107-AF)	TBD/96
7. Support Cometabolic Bioventing Demonstration (RTDF)	TBD/96
8. Support Surfactant Curtain Validation Study (AF S&T)	06/96
9. Resistive Heating Feasibility Demonstration (AF S&T)	10/96
10. Bioaugmentation Demonstration (SBIR PHII)	10/96
11. Bioremediation of Hydrazine (SERDP)	10/96

Established MOU with the DoD/Advanced Applied Technology Demonstration Facility's Rice Consortium to screen sites and technologies and plan experimental controlled release experiments.

Extensively reviewed and queried both the AF Center for Environmental Excellence data base and the Defense Evaluation and Support Agency's environmental data base for potential sites. Surveyed the Soil Conservation Service and Geological Survey for appropriate regional hydrogeologies Pre-selected seventeen bases that had potential for having the proper hydrogeological conditions and had characterization data on hand for further review. Surveyed each based by mail, telephone, then by site visits to review hydrogeology, base management acceptance, site accessibility, regulatory climate, state of site characterization, etc. Down selected four bases/sites for more extensive site survey prior to approval for establishing a SERDP National Test Site for DNAPL technologies.

After extensive site surveys, Dover AFB was chosen as the most acceptable location for the Groundwater Remediation Filed Laboratory (GRFL). Dover AFB management accepted the invitation to host the GRFL. The State of Delaware has expressed its willingness in writing to consider contained release experiments. Established management framework on site and at Armstrong Laboratory, Environics Directorate.

A full time on-site manager has been assigned to the Dover site. Extensive characterization has been completed, and Environmental Assessment has been written, coordinated, publicly reviewed, and a finding of no significant impact (FONSI) has been signed. Detailed characterization of GRFL site is complete. Construction of first test cell has begun. A peer Review Committee has been established for scientific review of incoming potential projects; an Installation Advisory Group has been groomed to review the practical and legal aspects of these efforts. A base support agreement and Memo of Understanding have been negotiated and signed. A comprehensive work planning document is in contractor preparation.

Project support, in addition to the ongoing characterization and infrastructure development, is being extended to a SERDP Pulsed Pumping project at Dover, AFB and is being provided to the EPA-RTDF Anaerobic Bioremediation Group, and research efforts are now in planning for field

demonstration. Have hosted a theme session at the '95 Geological Society of America annual meeting on Innovative Characterization of DNAPL Impacted Aquifers.

10. Transition Plan:

Cost and performance data will be collected by the standardized methodology and entered into the NETTS cost-and-performance database to be available by April 1996. At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	1,100	1,306	1,137	621	900	900	900	6,864

12. Performers:

An on-site Test Location Manager (TLM) is responsible to the Government Program Officer. The TLM will disseminate GRFL publicity material to potential demonstrators and provides professional guidance. A peer review group is formed to review the scientific merit of potential efforts coming to the GRFL. Arrangements have been made for utilizing the Installation Advisory Group (IAG) at Dover AFB as the vehicle for public involvement, regulatory input, and general local program review.

For purposes of coordination within the NETTS, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

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14. Keywords:

GRFL, DNAPL, Chlorinated Solvent, Contained Release, Fate and Transport, National Test Location, Technology Demonstration, Demonstration Site

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: National Environmental Technology Test Sites Program (NETTS) Air Force National Test Location for Chlorinated Hydrocarbons, McClellan AFB, Sacramento, CA

3. Agency: U.S. Air Force

4. Laboratory: Armstrong Laboratory, Environics Directorate, (AL/EQ)

5. Project ID: #861

6. Problem Statement:

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The National Environmental Technology Test Sites Program (NETTS) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in NETTS, and there are five test locations.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each NETTS test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each NETTS test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding (Army Environmental Center lead), the NETTS is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each NETTS test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

7. Project Description:

This project involves the preparation and management of demonstration sites at McClellan AFB, CA for innovative monitoring and remediation technologies for chlorinated hydrocarbons in soil and groundwater. The focus will be technologies for the treatment of soil gases and remediation process offgases. Ex situ processes for the treatment of groundwater will also be conducted.

The work will also include the development of a computerized data management system which will act as a repository for the cost and performance data from all NETTS demonstrations. The data management system will also inform other agency remediation managers of the status of the technology development. Decision matrices will be used to encourage other potential users of the technology.

8. Expected Payoff:

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each NETTS test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

Furthermore, the data management system will greatly assist in the transfer of technology from the research/demonstration sites to potential customers anywhere in the US or the world.

9. Milestones/Accomplishments:

A. Test Location Management/Infrastructure	
A1. Publicize and coordinate test site	09/94
A2. Update site characterization data	10/94
A3. Complete action plan for site development	12/94
A4. Site development for Offgas demonstrations	12/94
B. Demonstration Oversight	
B1. 2 -Phase Extraction	12/95
B2. High Voltage Electrical Application	10/95
B3. Flameless Thermal Oxidation	10/95
B4. Elastomeric Polymer Filter Media	12/95
B5. Vadose Zone Sensor	11/96
B6. Photocatalytic TIO_2	11/96
B7. Photolytic	04/96
B8. Silent Discharge Nonthermal Plasma	04/96
B9. Cometabolic	TBD
B10. Dual Phase Treatability Study	07/96
B11. Biofilter	09/96
B12. Gore Sorber Soil Screening Technology	07/96
B13. Acoustically Enhanced Remediation	08/95
B14. Radio Frequency Enhanced SVE	TBD
B15. Low Temperature Thermal Desorption	TBD
B16. Fenix Systems SVE Off-Gas Treatment	TBD
C. Database Development	
C1. Develop data model	09/95
C2. Develop first prototype	10/95
C3. Develop full prototype	12/95
C4. Install and operate data network	03/96

In FY95 McClellan AFB performed the administrative, logistic, and management functions necessary to establish the National Test Site. These activities included: test site infrastructure development, coordination with potential government, industry, and academic technology demonstrators. It also includes working with state authorities to develop a partnership for technology evaluation and possibly a state certification program. McClellan continues to work toward the goal of reciprocity with the Western Governor's Association.

During FY95 McClellan AFB also completed 5 technology demonstrations, began 5 additional demonstrations that are currently underway, and identified 7 potential demonstrations for the near future.

10. Transition Plan:

Cost and performance data will be collected by the standardized methodology and entered into the NETTS cost-and-performance database (when available). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
Test Location Management/ Infrastructure								
SERDP	570	194	0	335	500	500	500	2,599
Database Development								
SERDP	0	0	206	40	40	40	40	366
TOTAL SERDP	570	194	206	375	540	540	540	2,965

12. Performers:

12.1 Test Location Management. Demonstrations at McClellan AFB are managed by a Test Location Manager. On site execution and day-to-day oversight will be performed by a private firm contractor. The SERDP Program Office provides NETTS management and program oversight.

For purposes of coordination within the NETTS, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

12.2 Database Development. Database development is managed by a McClellan AFB staff manager. The work is performed by private firm contractors (Mitre Corporation) and government agencies (Sandia National Lab, EPA RREL)

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14. Keywords:

National Test Location, Chlorinated Hydrocarbons, Cost-and-Performance Database, Data Management

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: National Environmental Technology Test Sites Program (NETTS) EPA National Test Location for Bioremediation Research, National Center for Integrated Bioremediation Research and Development (NCIBRD), Wurtsmith AFB, Oscoda, MI

3. Agency: Environmental Protection Agency

4. Laboratory: Gulf Breeze Laboratory

5. Project ID: #864

6. Problem Statement:

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The National Environmental Technology Test Sites Program (NETTS) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in NETTS, and there are five test locations.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each NETTS test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off,

developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each NETTS test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding (Army Environmental Center lead), the NETTS is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each NETTS test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

7. Project Description:

The project objective is to establish, support, and operate the National Center for Integrated Bioremediation Research and Development (NCIBRD), a national field research and demonstration facility for advanced technologies for decontamination of hazardous wastes and remediation of spills and disposal sites. The facility has been established at the recently decommissioned Wurtsmith AFB in Oscoda, MI, and will serve as the EPA national test location in the NETTS program, addressing fuels and solvents problems, which are USAF-lead contaminants.

NCIBRD is addressing a broad array of research and development need pertaining to the transfer and conversion of laboratory findings into successful remediation practice. The program focuses on several specific problems relating to the development of core biotechnologies such as the enhanced understanding of microbiology and biochemistry, improved means for implementing biotechnology in engineering applications, and remediation of contaminated soils. The facility is focusing on technologies having evident promise for complete and cost effective remediation with minimal environmental disruption. These technologies involve on-site and in-situ processes which integrate enhanced biological technologies with the physicochemical techniques employed for contaminant source removal or control.

Controlled on-site research and demonstration programs dealing with advanced integrated technologies or decontamination of hazardous substances in wastes, soils, and groundwater are conducted at the facility. The majority of the contaminated sites at Wurtsmith AFB are already characterized at the remedial investigation (RI) level. Site characterization will continue as required to establish well-characterized physical, geochemical, and microbial background conditions at selected demonstration sites. These data are being shared with potential technology demonstrators for evaluation of site suitability for specific biotechnologies. Several of the sites are under hydraulic control by way of pump and treat systems. The facility provides a focal point

for coordination and cooperation within the broad community of institutions, agencies, and corporations currently attempting to develop these technologies.

8. Expected Payoff:

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each NETTS test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for reducing the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

NCIBRD provides significant direct and indirect benefit to the Department of Defense, Department of Energy, and the US Environmental Protection Agency environmental research and development programs. Advanced remediation technology research and demonstration results can be evaluated on a common performance baseline. This will ensure that the most cost effective technologies will be implemented for the remediation of thousands of contaminated military, public, and industrial sites throughout the country. NCIBRD also provides a standard test bed that environmental regulators can evaluate and accept. This will result in a simplified approval process for new technologies and the transfer of those technologies from the laboratory to the user. Field site testing at a location which is extensively characterized and controlled with monitoring well and other measurement systems will save considerable amounts of money in developing individual research projects. The Michigan Department of Environmental Quality and the University of Michigan provides matching funds to support NCIBRD and strongly supports the goals of the effort.

9. Milestones/Accomplishments:

A. Infrastructure Development

1. Test-location-wide site characterization database construction	4/95
2. Integrate database with GIS system and USAF BCA	7/95
3. Conduct site surveys for 5 prospective sites for in situ bioremediation	7/95
4. Conduct comprehensive survey/analysis of candidate Controlled Subsurface Injection sites	7/95
5. Design and obtain bids for construction	

of decontamination facility 4/95
6. Construct decontamination facility 6/95
7. Design system of parallel test cells for controlled subsurface injection of aqueous phase contaminants 12/95
8. Construction of first Test Cell for controlled subsurface injection (including monitoring and control systems) 4/96

B. Demonstration Oversight

1. Conduct demonstration of SCAPS tunable laser (729-A) 7/95
2. Conduct demonstration of Field GC-MS system (private vendor, assistance from NERL) 8/95
3. Start demonstration Ecological Biomarkers (244-EPA) 10/95
4. Complete second year of sampling and analysis program for intrinsic bioremediation demonstration at site FT-2 (405-EPA) 12/95
5. Complete initial sampling and analysis program for intrinsic bioremediation demonstration at site KC-135 (383-EPA) 3/96

NCIBRD has established the primary infrastructure, staff, and facilities to support evaluation and demonstration of site characterization and remediation technologies. The US Air Force Base Conversion Agency (BCA), EPA Region V, and the Michigan Department of Environmental Quality have approved NCIBRD's Quality Assurance Project Plan, Field Sampling Plan, and Health and Safety Plan. The Memorandum of Understanding and Right of Entry originally executed in 1993 between the USAF, BCA, and the University of Michigan have been updated for approval. NCIBRD's draft Test Location Management Plan is complete and has been submitted to the BCA for approval. NCIBRD leases seven buildings on the site and has lease applications pending for two more which will house a controlled injection test facility for in-situ technology trial. Field and laboratory support facilities have been established. In the past year, assistance has been given to four SERDP sponsored projects, five EPA projects, and two formal field demonstrations (i.e., field GC-MS and Laser Induced Fluorescence probe). Five additional sites have been characterized to judge their suitability for three potential USAF lead demonstrations of bioremediation technologies.

10. Transition Plan:

Cost and performance data will be collected by the standardized test plan methodology and entered into the NETTS cost-and-performance database (when available, McClellan AFB lead). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short

courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
Test Location Management/ Infrastructure SERDP	2,300	1,900	2,580	800	1,000	1,600	1,600	11,780

12. Performers:

EPA's National Center for Environmental Research and Quality Assurance has a Cooperative Agreement with the University of Michigan Department of Civil and Environmental Engineering, which is the lead institution in the NCIBRD Consortium, for technical management and execution of this project. The Consortium comprises EPA, DoD, University of Michigan, and the Michigan Department of Environmental Quality. It coordinates with representatives of academic research institutes, industrial corporations and associations (for example, through the Remediation Technologies Development Forum), and government agencies (through the Great Lakes and Mid-Atlantic Center for Hazardous Substance Research). Dr. Walter J. Weber, Jr., of the University of Michigan College of Engineering is the Executive Director of the Consortium. Dr. Michael Barcelona of the same institution will serve as the Operating Director of the Consortium. The Consortium maintains offices and staff in Ann Arbor, MI, and on the NCIBRD Test Location at Wurtsmith AFB. Demonstration activities are coordinated with the USAF Base Conversion Agency (BCA).

For purposes of coordination within the NETTS, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

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14. Keywords:

NCIBRD, National Test Location, Fuels, Solvents, Organic Mixtures, In Situ, Bioremediation, Technology Demonstration, Demonstration Site

SERDP FY96 PROJECT

1. SERDP Thrust Area: Cleanup

2. Title: National Environmental Technology Test Sites Program (NETTS) EPA National Test Location for Site Characterization and Monitoring Technology Demonstration Program

3. Agency: Environmental Protection Agency

4. Laboratory: National Exposure Research Laboratory, Characterization Research Division - Las Vegas (NERL, CRD-LV)

5. Project ID: #374

6. Problem Statement:

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The National Environmental Technology Test Sites Program (NETTS) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in NETTS.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each NETTS test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off,

developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each NETTS test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. The NETTS has nearly completed preparation of the developing Guidelines for Quality Technology Demonstrations which includes guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The Guideline is a common link among the Services and EPA to expedite the development and demonstration of better, more efficient technologies. EPA provides additional guidance and support to each NETTS test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

There is a clear need to ensure that better, faster, and less expensive technologies are available to those responsible for cleaning up contaminated sites. Achieving cost-effective site cleanup is in everyone's best interest. Currently there is a long lag time between the successful field demonstration of a new technology and its routine use. This will likely continue unless someone takes the lead in advancing innovative and emerging technologies. It is also apparent that without active involvement by EPA, the emergence and use of new technologies will continue only slowly. This project is considered a technology transfer and diffusion activity.

7. Project Description:

The purpose of this project is to sustain the EPA-led portion of the NETTS for facilitating the development, commercialization, and use of innovative monitoring, measurement and site characterization technologies. NERL, CRD-LV is responsible for planning and administering demonstrations of SERDP-developed technologies for site characterization and monitoring technology, as well as technologies funded by other sources (where the technology can be used to support a DoD requirement). NERL, CRD-LV is also responsible for producing guidance on how to conduct and evaluate these types of technologies, and for managing and disseminating information on demonstrated technologies. NERL, CRD-LV also provides general advice and support to the other NETTS National Test Location Managers for conducting demonstrations.

The FY96 resources will be used for supporting site characterization technology demonstrations and EPA's role in supporting the other National Test Location Managers. With regard to demonstrations, these resources will be used in FY96 to complete the demonstrations that were started in FY95 and to start additional demonstrations of SERDP-supported technologies. We have contacted the project officers identified in the FY94 SERDP Strategic Investment Plan to determine which technologies will require our support in FY96. We will identify those SERDP technologies that will be demonstrated in the subsequent quarterly reports. We are also in the process of identifying the technologies from other sources that may be suitable candidates for demonstration at the National Test Locations. These too will be identified in subsequent quarterly reports. However, we will seek the approval of the Technology Thrust Area Working

Group and SERDP Program Office before committing to a demonstration of non-SERDP derived technologies.

8. Expected Payoff:

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each NETTS test location provides opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

Savings in site cleanup will reduce the need for new or additional federal taxes to support federally funded cleanups. Lower costs for cleanups funded by private parties should reduce inflationary pressures. The demonstration program will provide a central conduit to channel new technologies to the marketplace more expediently than current methods. Investment capital should be easier to obtain because the developer will have a technology acceptance road map to show to investors. The verification of technology should help in reducing the amount of uncertainty that users often have regarding new technology to an "acceptable" level. We will support the use and implementation of new technologies by rapidly introducing them to the user community through training, field trials, and direct application to current sites. This demonstration activity satisfies many of the SERDP objectives. It is designed to maximize information transfer and reduce duplication; provide assistance to public and private sector users and developers; support the diffusion of technologies derived form basic R&D programs; be a collaborative effort; and support demonstrations of private sector technology demonstrations.

9. Milestones/Accomplishments:

	Planned	Resch.	Actual
1. Draft demonstration protocol	06/94		12/94
2. Draft data validation criteria	09/94		02/95
3. Demonstration plan technology #1	09/94		03/95
4. Draft information management plan	02/95	05/95	
5. Demonstration plan technology #2	02/95		02/95
6. Demonstration plan technology #3	04/95	05/95	05/95
7. Interim demonstration protocol	05/95	08/95	11/95
8. Final data validation criteria	05/95	05/96	

9. Demonstration report technology #1	07/95	02/96
10. Demonstration report technology #2	09/95	03/96
11. Demonstration report technology #3	10/95	04/96
12. Demonstration plan for SERDP funded technology	06/96	

- Distributed interim final version of the technology demonstration guidance
- Coordinated our activities with the Environmental Security Technology Certification Program
- Conducted a demonstration of technologies for the detection of metals in soils at the Western Environmental Technology Center in Butte, Montana
- Draft data evaluation guidance in review
- SCAPS demonstration occurred in May and second demonstration was conducted in November
- Field portable GC/MS demonstration was conducted at Wurtsmith AFB and Savannah River Technology Center
- Technologies for the detection of mercury in soil and sediments were demonstrated
- Contacted SERDP funded technology developers to determine those technologies ready for testing and those for demonstration
- Working with TTAWG on technology demonstrations for FY96
- Continued to promote the demonstration process within EPA to assist in acceptance of technologies by regulators

10. Transition Plan:

Cost and performance data will be collected and entered into the NETTS cost-and-performance database. At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short course/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

It is expected that the NERL, CRD-LV technology demonstration activity will be necessary through at least FY 03. This effort, in and of itself, will not be transitioned to others. Its function is to assist developers in transitioning their technologies into routine use.

11. Funding: $(K)

SERDP	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
	500	200	20	304	60	60	60	1,204

12. Performers:

The lead organization for this project is EPA. It will be administered by the Office of Research and Development's National Exposure Research Laboratory, Characterization Research Division in Las Vegas, NV. DOE's Sandia National Laboratory in Albuquerque, NM (SNL) is a partner in this activity. We are also working with Lockheed Environmental Systems & Technology Company (LESAT). LESAT is the NERL, CRD-LV mission support contractor. In DoD, the Navy's Naval Research Laboratory has become a member of the team. Their support is being provided by EPA through the Environmental Technology Initiative.

For purposes of coordination within the NETTS, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

13. Principal Investigator:

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14. Keywords:

Site characterization, Monitoring, National Test Location, Technology Demonstration, and Demonstration Site

TABLE
FY 1996 COMPLIANCE PROJECTS

	Funding $(K) FY96	ID Number	Page Number
Boiler/Engine Emissions			
Evaluation of Metal Perovskite Catalysts for NOx Reduction (AF)	75	177	CP-3
Compact, Closed-Loop Controlled Waste Incineration (N)	900	34	CP-8
Compact Waste Inceneration Demonstration (N)	500	887	CP-15
Non Thermal Plasma Technology for Reduction of Atmospheric Emissions (N)	500	1038	CP-19
Reduction of NOx Emissions from Marine Power Plants (N/EPA)	1000	42	CP-23
General Hazardous Waste Management			
Lead-Based Paint Hazard Mitigation (A)	700	521	CP-29
Emission Reduction Planning Model (AF)	200	175	CP-35
Laser Ablation/Ionization Characterization of Solids (DOE)	310	362	CP-40
Vapor Permeation VOC Recovery from Refueling and Storage (EPA/N)	400	252	CP-46
Monitoring			
Advanced Mass Spectrometry for Atmospheric Monitoring (AF)	400	192	CP-50
Leak Location in Underground Pipelines (EPA/A/N/NSF)	79	249	CP-56
Noise Impacts			
Reduction of Environmental Noise from Jet Engine Hush Houses (AF)	450	1051	CP-61
Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training (A)	285	523	CP-67

TABLE FY 1996 COMPLIANCE PROJECTS	Funding $(K) FY96	ID Number	Page Number
Open Burning/Open Detonation			
Characterization Open Burning/Open Detonation Emissions (A)	1,405	247	CP-73
Measuring and Modeling for OB/OD Permitting (EPA)	575	251	CP-78
Physical Treatment Processes			
Encapsulation of Hazardous Ions in Smectite Clays (DOE)	200	315	CP-82
Kinetics of Supercritical Water Oxidation (DOE)	460	364	CP-87
Waste Forms Based on Separations Media (DOE)	200	360	CP-93
Shipboard Emissions			
Shipboard Non-Oily Wastewater Treatment System (N)	450	29	CP-99
Waste Minimization/Recycling			
Evaluation of the Use of Waste Energetics as Supplemental Fuels (A/N/DOE)	495	524	CP-104
Compliance Total	9,584		

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Evaluation of Metal Perovskite Catalysts for NOX Reduction

3. **Agency:** U.S. Air Force

4. **Laboratory:** Armstrong Lab (AL)

5. **Project ID:** #177

6. **Problem Statement:**

Goal: The goal of this research is to investigate whether oxygen deficient strontium-lanthanum cobaltate ($Sr_XLa_{1-X}CoO_3$) can be stabilized for long-term use as a catalyst for reduction of oxides of nitrogen (NO_X).

Background: The control of NO_X emissions is mandated by federal, state, and local regulations. These sources are generally characterized by high-temperature combustion of fossil fuels, where organically bound nitrogen in the fuel oxidizes to form NO and small amounts of NO_2 and N_2. (In most cases, NO_2 emissions will be as low as 5-10 percent by volume of total NO_X emissions.) While fuel combustion to produce commercial power and motor vehicle emissions are the two largest contributors in the United States to NO_X production, other sources have been targeted as well, including jet engine test cells (JETCs). Existing methods to remove NO_X from combustion exhausts do so only under a narrow range of conditions.

Previous investigations have shown that NO can be reduced by levels greater than 90 percent by $LaCoO_3$ catalysts. Conversion of NO increases from less than 10 percent at temperatures below about 450°C to over 90 percent at about 525°C for internal combustion engine exhausts with air-to-fuel ratio of 12.85. At 660°C, an air-to-fuel ratio of 14.35 resulted in 90 percent conversion of NO (excess air requires higher conversion temperatures). Stability can be expected at relatively higher temperatures, as $LaCoO_3$ has a melting point of 1607°C, and the La--Co--O system has a low temperature eutectic in air at 1482°C. The presence of CO in exhaust air enhances the conversion of NO while O_2 reduces NO conversion. CO reacts with H_2O and produces H_2, which at sufficiently high temperatures, acts to reduce the $LaCoO_3$ catalyst, resulting in an oxygen deficient structure. This oxygen vacancy allows for chemisorption of CO or NO, and likewise acceleration of the conversion reaction of NO and CO to N_2 and CO_2. As the conversion process continues, the $LaCoO_3$ is reduced through a complex series of reactions, which are accelerated in the presence of O_2. At weight losses above 3.5 percent, phase changes begin to occur and Co metal is formed, resulting in loss of catalytic activity. The addition of a Sr ion by replacing one La ion (yielding $Sr_XLa_{1-X}CoO_3$) may result in a faster and lower temperature conversion of NO, while withstanding higher levels of reduction before losing effectiveness as a catalyst. Previous investigations suggest that the $Sr_XLa_{1-X}CoO_3$ catalyst can withstand weight losses of between 8-9 percent before reverting to Co metal.

Concentrations of selected species (such as oxygen) during reactions can be monitored using electrochemical cells. By controlling the oxygen concentrations, the reduction of the catalyst can be controlled.

7. Project Description:

Technical Objective: The technical objective of this project is to investigate the thermodynamics and kinetics of reduction of $Sr_xLa_{1-x}CoO_3$ in NO and determine the limits of stability of the active oxygen deficient phase to establish the effectiveness of $Sr_xLa_{1-x}CoO_3$ for use as a long-term NO_X catalyst. Representative NO environments containing gases which can be expected in exhaust streams of interest (e.g., JETCs) will be used.

Technical Approach: All basic research for this project will be on the laboratory scale, including modeling of representative exhaust streams. (1) The thermodynamics and kinetics of reduction of $Sr_XLa_{1-X}CoO_3$ will be analyzed using techniques involving thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and the use of high-temperature electrochemical cells to measure oxygen activity. X-ray diffraction techniques will be used for crystallographic examinations. Models for thermodynamic and kinetics of phase equilibria of the oxygen deficient phase will be developed. (2) Developing techniques for stabilizing the oxygen deficient phase will involve investigating effects of varying stoichiometry on stability of the ceramic material and examining the feasibility of using solid state electrolytes (YSZ) to control the extent of reduction of the catalyst. Once a technique to stabilize the active phase has been developed, the kinetics of conversion of NO will be investigated to determine efficiency and speed of catalysis of NO. (3) Models of the catalysis of NO by $Sr_XLa_{1-X}CoO_3$ will be developed and reported.

Future technology demonstration if funded will be performed at an Air Force facility. Tyndall AFB FL and McClellan AFB CA are potential candidates. (1) Technical data required for installation of the slipstream and full-scale emission control systems will be gathered. Prior experience and information gained from related projects will be beneficial in completing this task. (2) A sub-scale system will be designed and installed to evaluate performance of the catalyst under near-full scale operating conditions. A multigas analyzer in conjunction with a computer data acquisition system will be utilized to provide continuous emissions monitoring during testing. (3) Results from the sub-scale prototype system will be evaluated and reported. These results will be used in the design of a full-scale prototype control system for a JETC. (4) The control system will remain in use for a sufficient time to determine the long-term stability and life cycle of the catalysts. The same data acquisition system will be utilized. (5) Test results will be evaluated and reported.

Relationship to DoD Environmental Objectives: This research, as applied to DoD JETCs, directly contributes to the requirement to control maintenance process emissions as identified in the Tri-Service Environmental R&D Strategic Plan, DoD Pillar 2: COMPLIANCE; Requirement Thrust 2.B.2: Maintenance Process Emissions (Test Stands and Cells).

Relationship to Other Work: This is an alternative approach applicable to NO_X removal from JETCs. A Small Business Innovative Research (SBIR) program initiated seven independent approaches to NO_X control for JETCs and identified one, a vermiculite--MgO sorbent process, as the most practical and cost-effective at present state of development. Promising technologies such as the $Sr_XLa_{1-X}CoO_3$ catalyst should be pursued as a potential marketable NO_X reducer and replacement NO_X control for JETCs in the event the vermiculite--MgO sorbent fails as a practical control device.

Technical Risks: There are some limited risks in this research. It may be difficult to control the degree of reduction of the catalyst, precluding long-term use. In addition, the catalytic activity of strontium-doped lanthanum cobaltate may be too slow to act as a fast catalyst needed for current applications.

8. Expected Payoff:

Potential Users: Air Force major command operations and maintenance activities that emit combustion exhausts, other DoD operations and maintenance activities, and private operations could benefit from this research.

Impact: If successful, this work can lead to effective and inexpensive catalysts for NO and CO conversion. The catalyst has the potential to benefit many applications with high-temperature NO_X reduction, including JETC emission controls, and possibly direct emissions from jet engines and combustion sources. $Sr_XLa_{1-X}CoO_3$ has a relatively low concentration of strategic materials and applications where $Sr_XLa_{1-X}CoO_3$ could replace platinum may be identified.

9. Milestones/Accomplishments:

1. Materials Preparation	09/94
2. Design and Construction of Testing Apparatuses	02/94
3. Investigate Thermodynamics and Kinetics of Reduction of Oxygen Deficient Phase	09/95
4. Phase I Final Report	10/95
5. Identify Techniques to Stabilize the Oxygen Deficient Structure	03/96
6. Investigate the Kinetics of NO Reduction by Stabilized $Sr_XLa_{1-X}CoO_3$	09/96
7. Phase II Final Report	10/96
8. Complete Investigations and Development of Models	09/97
9. Final Report	10/97

Pure $LaCoO_3$ as well as strontium doped $LaCoO_3$ catalyst materials were prepared by typical ceramic processing methods. A bench scale laboratory apparatus capable of high temperature (>1300°C) electrochemical measurements was designed and constructed for the evaluation of the high temperature properties of catalyst materials. Thermogravimetic analysis (TGA), differential thermal analysis (DTA), differential scanning calorimeter (DSC) and x-ray

diffraction (XRD) were used to determine the thermal and compositional stability of the catalyst materials in simulated JETC exhaust gases. Cation deficient perovskites were found to be chemically and structurally more stable than the stoichiometric composition in simulated JETC exhaust gases. The composition $(Sr_{0.3}La_{0.7})_{0.9}CoO_{2.715}$ was identified as the composition to be pursued for further investigation based on thermodynamic stability and electrocatalytic activity. It was found to be compositionally stable up to 1300°C in a simulated JETC exhaust atmosphere.

10. Transition Plan:

The results of this research will be used if funded in future 6.3 technology demonstration effort where catalyst performance in controlling emissions from an operational JETC will be demonstrated at an Air Force facility. Favorable results would allow technology transfer to the Propulsion System Program Office at Wright Laboratories for engineering manufacturing development (EMD) and fielding. Technical reports and articles will also be produced for the R&D community, other agencies, and industry.

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	TOTAL
SERDP	175	25	75	90	365

12. Performers:

This is a joint research effort between: Air Force Armstrong Laboratory Environics Directorate, Environmental Compliance Division (AL/EQS); and Army Construction Engineering Research Laboratories (USACERL). Research will be conducted by USACERL and if funded field-demonstrated in the future at an Air Force facility.

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14. Keywords:

Perovskite, NOX, Air pollution, Catalyst, Doping, Cintering.

SERDP FY96 PROJECT

1. SERDP Thrust Area: Compliance

2. Title: Compact, Closed-Loop Controlled Waste Incineration (Development)

3. Agency: U.S. Navy

4. Laboratory: Naval Air Warfare Center Weapons Division, China Lake, CA 93555-6000

5. Project ID: #34

6. Problem Statement:

A new generation of incinerators, which can be based in part on recently developed active ramjet-combustion control, is required for ship-board waste disposal to enable Navy ship access to ports and bodies of water around the world without operational constraints related to environmental laws and regulations. The present practice of over-board discharge and storage/off-loading will be unacceptable. Thermal destruction is considered the ultimate solution beyond 2000 for all types of waste, including trash, garbage, plastics, medical and hazardous wastes. The need for improved waste disposal is clearly identified in the Tri-Service Environmental Quality R&D Strategic Plan. For the future incinerators, a new technology has to be developed which will allow assured waste destruction in a compact design. This technology is not only applicable to a new type of generic solid and liquid waste incinerator consisting of a primary chamber (solid/liquid waste decomposition) and secondary chamber (afterburner), but in particular to two types of incinerators of current Navy interest, namely the afterburner of the proposed plasma arc thermal destruction system and the solid sludge vortex incinerator. The latter system incinerates black and gray water derived sludge in a vortical flow which is different than the vortex flow investigated in the SERDP program.

Present commercial incinerators are typically unsuitable for Navy shipboard installation and operation because they are oversized and often do not meet incineration standards, in particular at off-design operation with the waste mass flow above design conditions. Oversizing in present systems, in terms of air and auxiliary fuel mass flows, reactor size, and air pollution control systems is necessary because physical understanding of interrelated processes in mixing and combustion is limited and control authority over the various detailed physical steps which make-up the incineration process does not exist. Present control of incinerators is based primarily on changing the waste and oxygen mass flows using time-averaging, intrusive sensors without controlling the underlying physical processes. The new type of incinerator will use non-intrusive, real-time and continuous sensing of the exhaust species. This information is then used in a feed-back loop via a controller to actively alter critical incineration steps in the primary and secondary chamber.

Potential development of these advanced incinerators is made possible through recent accomplishments in combustion control which is based on the detailed understanding of

acoustic/fluid dynamic/combustion interactions. With this new technology, significantly improved waste destruction efficiencies and increase in waste mass-flow levels have been demonstrated for solid and gaseous/liquid wastes. This new technology was first explored in an ONR sponsored research program (FY93 to FY95) and under EPA sponsorship. In the ONR research with gaseous and liquid wastes, the waste destruction efficiency was improved several order of magnitudes using synchronized fuel/waste injection into reacting periodic vortices and waste injection into recirculation zones, which were trapped between a sudden dump and the contraction to the combustor exit. In the EPA sponsored research using hazardous and municipal solid waste surrogates in a rotary kiln, excited resonant acoustics reduced the magnitude of the generated "puffs" and soot emission, and increased the waste mass flow rate by 30 percent without changing the exhaust gas properties.

The SERDP program to explore this new technology for compact, ship-board incinerators was started with FY94 funding. The initial goal was to develop the technology basis for a new generic two-chamber system with solid waste decomposition in the primary chamber and afterburning in the secondary chamber. It was estimated that the volume can be reduced by a factor of 4 to 5 by using resonant acoustics in the primary chamber and periodic or trapped vortices in the afterburner. Starting in FY96 the compact incinerator program will be continued in two separate, however closely related programs, referred in the following as S&T and Demonstration programs. The S&T program (SERDP ID#34) is a continuation of the original SERDP program to develop the necessary science & technology basis for this new type of incinerator, while the Demonstration program (ID#887) titled Demonstration of a Compact, Closed-Loop Controlled Waste Incinerator will apply this new technology to two specific Navy incinerator programs, namely the proposed plasma arc thermal destruction system and the sludge vortex incinerator which is being upgraded for increased waste mass flow. The continuation of the compact incinerator effort in two separate programs assures that the technology is applied to specific military needs at an earlier time than originally planned.

The S&T program described here will continue to establish the basis of using resonant acoustics for enhanced waste pyrolysis (with emphasis on sludge incinerator) and controlled vortex dynamics for enhanced and controlled afterburning (as related to a plasma arc incinerator). The afterburning process will be closed-loop controlled which will be accomplished with newly developed control components, including new diode-laser based sensors for real time and continuous emission monitoring, new types of actuators, and a non-standard controller based on fuzzy logic and neural nets. These continuing S&T studies are required for the technology demonstration which will be accomplished in two phases. In the first phase a Process Development Unit with existing control components will be used. In the second phase an Integrated Prototype with advanced control components will be used which are being developed in S&T program.

7. Project Description:

The overall goal of the S&T program is to develop the necessary technology to apply the new compact-incinerator technology to Navy incinerator systems. This approach for achieving assured pollution-free waste destruction in a compact system requires the physical understanding of the

various steps in the incineration process, the determination of appropriate control parameters to actively influence the underlying physical processes, and the use of sensors, a controller, and actuators to continuously monitor and modify the waste incineration processes in a closed-loop fashion.

The S&T studies will be done in two tasks: (1) control component development; and (2) sub-scale evaluation and integration.

(1) Control Component Development:
The development is divided into four tasks, namely the development of advanced sensors and actuators, a process model, and an adaptive controller.

Sensors - Active combustion control for incinerators requires sensors in two main categories: real time and continuous monitoring. Real time monitoring (for example of temperature) will follow the development of periodic vortices; continuous monitoring (for example of toxic emissions) will adapt control parameters (for example phase between vortex development and waste injection) for assured destruction. The tunable diode laser absorption spectroscopy technology is being extended to apply this technology to different exhaust species and to refine the data reduction techniques and computer control procedures for rapid system analysis and real time monitoring.

Actuators - Actuators will be developed using the new RAINBOW piezoelectric material and the new Terfenol magnetostriction alloy for mass-flow modulation. Work is aimed on scale-up to the requirements of the demonstrator and detailed performance characterization of the actuators for mass flow, pressure drop, frequency response, modulation amplitude, and reliability.

Process Model - State-of-the-art process models are unable to predict the unsteady nature of the new closed-loop controlled incinerator. It is necessary to replace in these models time-independent coefficients with time-dependent ones. The data from Large Eddy Simulation (LES) will be statistically time-averaged and spatially averaged to obtain simplified empirical relations for the parameters of interest. The newly developed process models will be used to determine effects related to geometry, scale, chemistry path ways, radiation, and failure modes. This type of modeling is also necessary for the development of the controller.

Controller - Implementation of active control requires the development of a control model. In the absence of a combustion model, conventional control algorithms, even when using the most advanced plant identification techniques, are not suitable for the proposed demonstration. Two approaches of control modeling will be pursued, namely neural nets and fuzzy logic. Neural nets require a mechanistic understanding of the incineration process to effectively implement the learning process, but a combustion model description is not necessary. Fuzzy logic is not based on precise relationships between input and output, but on imperfect rules which will be developed from combined LES modeling and experiments.

(2) Sub-scale Evaluation and Integration:
Sub-scale experiments with advanced laser diagnostics will be continued to: (1) evaluate

concepts; (2) validate control components; and (3) integrate control components.

Concept evaluation - The general concept of a compact incinerator has been defined with resonant acoustics for enhanced pyrolysis of solid (sludge) waste in the primary chamber, and controlled vortex combustion for enhanced afterburning in the secondary chamber. Additional work is required to evaluate the trapped vortex concept and to provide insight into sludge spray incineration in an acoustic field.

The effect of acoustics on solid waste has been documented and the enhancement of the incineration process demonstrated. It is expected that the acoustics will also enhance incineration of sludge; however, to optimize the enhancement of sludge incineration in an acoustic field, additional S&T work is required to investigate the effect of the acoustics on spray incineration and determine optimum design parameter.

For enhanced afterburning performance, periodic vortices and trapped vortices are considered. Design criteria for the periodic-vortex concept have been established and are readily applicable to the conceptual design of an afterburner for the plasma arc system. Additional work is needed to determine design criteria for the trapped-vortex concept, which will be accomplished with existing models recently developed for a new gas turbine concept. The modeling effort uses the General Electric Aircraft combustor design code CONCERT and a direct numerical simulation (DNS) code. The DNS code is an axisymmetric time dependent simulation with combustion. It will be used to determine the size of the cavities for trapping a vortex in combusting flows. Once the cavity sizes are determined, the 3D code CONCERT will be used to investigate the locations of the fuel and waste injection points for different configurations.

Control component validation - The sub-scale test-rig will be used to validate the control components to be developed, and requirements for full-scale demonstration will be defined.

Control component integration - The same sub-scale test rig will be used to integrate the control components and to study the interactions between the primary and secondary chamber. Issues related to the flow dynamics and acoustics will be addressed. Both the trapped-vortex and periodic-vortex concepts will be investigated. Specific attention will be given to particulate (soot) formation and combustion. Aerodynamic particle traps and reactive filters will be studied to assure particulate burn-out in the vortex-dominated afterburner. For afterburning in periodic vortices, closed-loop active control will be tested. Diode laser based sensors, new types of actuators, and an adaptive controller based on neural nets or fuzzy logic will be integrated. The control system will be tested for varying waste types and mass flows. Also, the ability and robustness of the system will be determined to actively control the incinerator process in response to continuous measurements of hazardous exhaust species. The effectiveness of the new closed-loop controlled system will be compared to existing incinerator technologies in terms of compactness and emission characteristics.

8. Expected Payoff:

Successful demonstration of a compact incinerator with real-time exhaust monitoring for active combustion control represent a significant step towards assured waste incineration. Active combustion control will be scaled-up from laboratory flame experiments to combustor experiments (scaling factor of 15) using novel sensors, actuators, and controller. The compact-incinerator technology, which will be developed, will be demonstrated for ship-board application in a separate program, and will be essential for the development of environmentally sound ships beyond the year 2000. Compact incinerators are also desirable for on-shore use in the government and private sector. Small, compact incinerators will allow on-site waste destruction and avoid waste transportation to large incineration sites. In particular, medical waste incineration is a prime candidate in the private sector for a compact system. The closed-loop active control of the incineration process will for the first time assure proper incineration during design and off-design operation. Successful demonstration of the assured waste incineration on-board ships will result in significant cost savings by avoiding cost, for waste off-loading and on-shore destruction, in particular in foreign countries.

9. Milestones/Accomplishments:

FY96 Milestones

1. Requirements for Process Development Units defined	01/96
2. Studies on vortex entrainment through boundary layer interactions completed	04/96
3. Effect of acoustics on solid phase heat transfer mechanism determined	04/96
4. Effect of acoustic excitation on t-v combustor performance determined	04/96
5. Primary/secondary chamber interaction studies completed	07/96
6. Particle effects on afterburning determined	09/96
7. Advanced actuator design completed	08/96
8. Neural net cost function and "learning" procedures defined	09/96
9. Fuzzy logic rules defined	09/96
10. Set-up for sludge-spray/acoustic interaction studies completed	09/96
11. Sub-scale t-v afterburner concept evaluation completed	09/96
12. Capability of diode laser sensor for real-time temperature control in afterburner demonstrated; novel laser source for mid-IR identified	09/96

FY97 Milestones

1. Requirements for Integrated Prototype demonstration completed	01/97
2. Fuzzy logic controller applied to LES model and experiments	09/97
3. Diode laser extended to mid IR to monitor CO and C6H6	09/97
4. Actuator performance for full-scale evaluation demonstrated	09/97
5. Sub-scale integration of new control components completed	09/97
6. Mechanism of sludge incineration in acoustic field identified	09/97
7. Sub-scale trapped-vortex afterburner optimized	09/97

FY98 Milestones

1. Sensor system development completed 03/98
2. Sub-scale closed-loop, active control experiments completed 03/98
3. Full-scale requirements for sensors and controller defined 03/98

FY94/95 Accomplishments

Scale-up validity of periodic-vortex flame experiments demonstrated. Interactions between acoustics and flow instabilities of main air and auxiliary fuel identified. Feasibility of periodic-vortex afterburner demonstrated.

Large Eddy Simulation (LES) adapted to scale-up facility for parametric studies of the effect of changing geometry, waste type, and other relevant parameters. Engineering design model developed from time-averaged LES data. Fuzzy control method based on engineering model initiated.

For the trapped-vortex afterburner demonstrated that both the DSN and CONCERT codes can be used to determine the optimum size of a cavity that will trap a vortex for a non-combusting flow.

Multiplexed diode laser measurements along a common fiber-optics path performed for H2O, CH4, NO2, and temperature. Achieved kilohertz (frequency scanning) and 1 megahertz (constant frequencies) temporal resolution.

Periodic modulation demonstrated for main air flow (electro-pneumatic valve and Rainbow high deflection piezoelectric ceramics) and for liquid fuel (magnetostriction Terfenol-D alloy and electromagnetic valve).

Afterburner for plasma thermal destruction system and sludge incinerator for technology demonstration selected.

10. Transition Plan:

The SERDP program is coordinated with Naval Surface Weapons Center-Carderock Division (NSWC-CD) to apply the new combustion control technology to (1) sludge incinerator upgrade for increased throughput and waste stream flexibility (Gordon Smith) and (2) afterburner of plasma are waste destruction system for compact, efficient design (Gene Nolting and Mike Kelly). Regular Meetings with NSWC-CD and their industrial contractors will be held. In addition dual-use applications will be explored with manufactures of medical waste and small municipal combustion systems (Consumate, Simonds, Bio-Oxidation), and manufactures of thermal equipment for ship-board application (Westinghouse, GE, General Dynamics, Bath Iron Works).

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	FY98	TOTAL
SERDP	700	300	900	600	500	2,190

12. Performers:

Performers are: Naval Air Warfare Center Weapons Division (NAWCWPNS), Georgia Institute of Technology, Stanford University, Air Force Wright Laboratories, and Energy and Environmental Research Corporation (EEC). In FY96 funding will be also provided to University of California, Los Angeles (UCLA) and University of Colorado to complete the ONR funded research with SERDP-project specific tasks.

13. Principal Investigator:

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14. Keywords:

Incineration, compact design, active combustion control, real-time monitoring, closed-loop control, acoustic/fluid dynamic/combustion interactions.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Demonstration of Compact, Closed-Loop Controlled Waste Incinerator

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Air Warfare Center Weapons Division, China Lake, CA 93555-6001

5. **Project ID:** #887

6. **Problem Statement:**

The need for the next generation of marine incinerators, which combine high performance with extreme compactness, are described in SERDP project "Compact, Closed-Loop Controlled Waste Incinerator" (Project ID #34). This project also describes the underlying principles and concepts for the new compact-incinerator technology, which includes excited resonant acoustics for enhanced solid/liquid waste pyrolysis and actively controlled vortex combustion for enhanced afterburning. The SERDP compact-incinerator project was started with FY94 funding. The initial goal was to develop the technology basis for a new generic two-chamber system with solid waste decomposition in the primary chamber and afterburning in the secondary chamber. Starting in FY96 the compact incinerator program will be continued in two separate, however closely related programs, referred in the following as S&T and Demonstration programs. The S&T program is a continuation of the original SERDP program to develop the necessary science & technology basis for this new type of incinerator, while the Demonstration program, which is described here, will apply this new technology to two specific Navy incinerators, namely a plasma arc thermal destruction system, which is being explored by the Navy for ship-board incineration, and a sludge incinerator, which is being upgraded for increased waste mass flow. The continuation of the compact incinerator effort in two separate programs assures that the technology is applied to specific military needs, which are described in more detail in the following, at an earlier time than originally planned.

For the thermal treatment of black liquor sludges, the Navy is using the "vortex" incinerator. The sludge is injected into a single combustion chamber. An air assisted nozzle is used to atomize the sludge so that a spray of sludge is introduced. An auxiliary fuel burner is used to introduce high temperature hot gases in a tangential orientation to the same chamber. the resulting vortical flow is different than the controlled vortex flow developed for controlled combustion in the SERDP program. These black water sludge vortex incinerators are rather simple combustion devices whose performance will likely not meet new sewage sludge incineration regulations for organic emissions and particulate control. In addition, these devices are limited in their ability to achieve high throughput rates due to the short combustion residence times in the chamber and the relatively long burn out times associated with sludge droplet combustion. The resonance acoustics concepts under development in the SERDP S&T program has the potential to dramatically improve the performance of these devices by enhancing the rate of combustion of

the sludge droplets and therefore allowing better organic combustion and higher throughput rates.

The plasma arc treatment of solid waste is currently pursued by the Navy as compact high performance systems for ship board operation. The plasma arc process pyrolyzes the solid waste with an electrical arc discharge in a primary chamber and generates a pyrolysis gas. These systems will need to be integrated with a high performance compact afterburner system in order to take full advantage of the features of the plasma arc primary chamber. The actively controlled vortex combustion concept under development in the SERDP S&T program is directly amenable to the afterburning of the pyrolysis gases through the controlled pulsation of the combustion air and the proper introduction of the pyrolysis gases into the vortex structures generated ;by the pulsations. Also, the trapped vortex concept has the potential for high performance and compactness.

7. Project Description:

The SERDP S&T activities will be reviewed and concepts for a practical embodiment will be developed to apply the new technology to the sludge vortex generator and the plasma system afterburner. The demonstration will be carried out in two phases. First, the current S&T technologies will be used for the feasibility demonstration using Process Development Units (PDUs). This demonstration will use recently developed control components, which include standard actuators and sensors, and a simple time-delay controller. Subsequently, the emerging results from the current SERDP S&T work will be used for the Integrated Prototype demonstration with advanced sensors and actuators, and an adaptive controller. The performance of the new compact incinerators will be compared with alternative disposal options (both current and other possible technologies); the relative advantages and disadvantages will be compared.

The project is divided into 13 tasks to accomplish the technology demonstration in the two phases. The tasks include (1) Active Control Concept Definition, (2) Strawman Active Control Design, (3) Complete Design of the Process Development Units (PDUs) for Plasma Afterburner and Sludge Incinerator, (4) Equipment Procurement and Modification, (5) Demonstration Testing which include exploratory experiments with advanced laser diagnostics, (6) Engineering Analysis and Evaluation, (7) PDU Demonstration Reporting, (8) Integrated Prototype Design, (9) Construction of Integrated Prototype of Compact Incinerator, (10) Demonstration Testing of Prototype, (11) Engineering Analysis and Evaluation, (12) Performance Comparison, (13) Prototype Demonstration Reporting.

8. Expected Payoff:

Successful demonstration of a compact incinerator with real-time exhaust monitoring for active combustion control represent a significant step towards assured waste incineration and can be the basis for the next generation incinerators. For the first time, active combustion control will be scaled-up from laboratory flame experiments to full-scale demonstration units (scaling factor of 100) using novel sensors, actuators, and controller. The compact-incinerator technology which will be developed will be demonstrated for specific ship-board application, and will be essential for the development of environmentally sound ships beyond the year 2000. Compact incinerators

are also desirable for on-shore use in the government and private sector. Small, compact incinerators will allow on-site waste destruction and avoid waste transportation to large incineration sites. In particular, medical waste incineration is a prime candidate in the private sector for a compact system. The closed-loop active control of the incineration process will for the first time assure proper incineration during design and off-design operation. Successful demonstration of the assured waste incineration on-board ships will result n significant cost savings by avoiding cost for waste off-loading and on-shore destruction, in particular in foreign countries.

9. Milestones/Accomplishments:

FY96 Milestones

1.	PDU demonstration design completed	02/96
2.	PDU demonstration test plan completed	03/96
3.	Exploratory PDU experiments with laser diagnostics completed	05/96
4.	PDU experiments completed	07/96
5.	PDU demonstration completed	09/96

FY97 Milestones

1.	Integrated Prototype (IP) design completed	05/97
2.	IP demonstration test plan completed	08/97
3.	IP fabrication completed	09/97
4.	Exploratory IP demonstration tests with laser diagnostics completed	09/97

FY98 Milestones

1.	Support experiments with laser diagnostics completed	04/98
2.	IP demonstration completed	05/98
3.	Final report completed	09/98

10. Transition Plan:

The SERDP program is coordinated with Naval Surface Weapons Center-Carderock Division (NSWC-CD) to apply the new combustion control technology to (1) sludge incinerator upgrade for increased throughput and waste stream flexibility (Gordon Smith) and (2) afterburner of plasma arc waste destruction system for compact, efficient design (Gene Nolting and Mike Kelly). Regular meeting with NSWC-CD and their industrial contractors will be held. In addition dual-use applications will be explored with manufacturers of medical waste and small municipal combustion systems (Consumate, Simonds, Bio-Oxidation), and manufactures of thermal equipment for ship-board application (Westinghouse, GE, General Dynamics, Bath Iron Works).

11. Funding: $(K)

	FY96	FY97	FY98	TOTAL
SERDP	500	900	700	2,100

12. Performers:

Performers in the demonstration program are Environmental Research Corporation (EEC) and Naval Air Warfare center Weapons Division (NAWCWPNS). Work will be performed by EEC, except for the exploratory PDU experiments using advanced laser diagnostics which will be performed by NAWCWPNS.

13. Principal Investigator:

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14. Keywords:

Incineration, prototype, demonstration, compact design, active combustion control, real-time monitoring, closed loop-control, acoustic/fluid dynamic/combustion interactions.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Non Thermal Plasma Technology for Reduction of Atmospheric Emissions

3. **Agency:** Department of Energy

4. **Laboratory:** Los Alamos National Laboratory

5. **Project ID:** #1038

6. **Problem Statement:**

Goal: Our main goal for Years 1-3 of this effort is to evaluate and develop non-thermal plasma (NTP) reactor technology for the reduction of atmospheric emissions. The primary emphasis is on NOx and HAPs (hazardous air pollutants); a secondary emphasis is on specialized VOC (volatile organic compound) applications. The main goal of Year 4 is a field-pilot demonstration of NTP equipment. Inherent in these goals is a rigorous technology comparison (e.g., discharges & electron beams), the formulation of engineering scaling criteria and algorithms, demonstration of operational effectiveness, and provision of a basis for selecting the most appropriate NTP technology for DoD applications.

Background: Because of a greater emphasis on environmental issues, increasing regulations, and increased scrutiny by regulators, there is a growing need to control the emission of oxides of nitrogen (NOx) and HAPs) - including volatile organic compounds (VOCs) at DoD installations. These emissions are frequently episodic (e.g., jet engine test cells (JETCs); painting, stripping and cleaning operations) and variable, with toxic gas loadings spanning a large concentration range from parts-per-million (ppm) to parts-per-thousand (ppt). Optimal existing technologies for high destruction-efficiency Nox and HAP/VOC control suffer from significant drawbacks. Both high temperature (incineration) and medium temperature (catalytic) oxidation are quite costly and produce large amounts of global warming gases such as CO_2 as well as unwanted combustion byproducts. Filter techniques have problems of saturation and ultimate disposal of the filter media. Electric-discharge driven NTPs are emerging as potentially very attractive candidates for NOx and HAP/VOC emission control due to the relative simplicity and potential flexibility of the NTP reactors. These plasmas can remove multiple pollutants over a wide range of flow rates (with banks of reactors in parallel). Electron-beam driven NTPs seem quite attractive due to the efficient production of energetic electrons. However, their applicability for treating relatively small flows of contaminated air is questionable due to the present high cost of e-beam equipment. The development of smaller and lower-cost e-beam sources is not a present reality and further work is still required in developing long-life, vacuum-gas separation windows. These are a number of cases of the use of NTP-based devices for application such as NOx and SOx control in flue gases, NOx control from diesel engines, air purification in automobile tunnels, removal of pollutants from contaminated soils, and the secondary treatment of off-gases from thermal units. However, present experience has shown that each different NTP reactor (e.g., pulsed

corona, barrier discharge, e-beam, etc.) has unique characteristics with respect to target gas destruction, electrical efficiency, and propensity for toxic byproduct formation, depending on its design and electrical characteristics. These issues must be resolved and scaleable, optimized reactors must be pilot tested to informatively choose the most appropriate NTP technology for DoD applications.

7. Project Description:

Technical Objective - Our overall project objective is to evaluate and develop NTP reactor technology for DoD air emissions control applications. A key goal is to provide a basis for detecting the most appropriate NTP technology for DoD applications by evaluating the performance of prototype and pilot-scale NTP reactors (corona, dielectric barrier, electron beam) for NOx and HAP abatement and specialized-VOC control (should other technologies prove inadequate or emission standards become more stringent) and to assist in the commercialization of the technology. This will be accomplished by (1) developing a predictive, reactor simulation model for use in prototype development and scale-up; (2) by experimental verification of the modeling results; and (3) formulation of engineering scaling and optimization criteria and the use of these in the demonstration of scaleable laboratory-pilot and field-pilot reactors. The development of an efficient reductive-mode NOx processor is a key goal.

Technical Approach - To meet our technical objectives, we plan a four-year effort starting with technology assessment and laboratory evaluation tests, progressing through laboratory pilot equipment optimization and scaling and culminating in the development of NTP technology selection criteria, based upon field-pilot testing. In the first year a comparative assessment of electric-discharge driven and electron-beam driven NTP reactors will be performed, reaction kinetic models will be developed, and experiments for issue resolution will be designed. In the second year reactor scaling criteria and optimization models will be developed and scaling studies will be initiated with laboratory-pilot apparatus. In the third year, reactor scale-up, optimization, and system engineering will be completed to the point of starting the designing of a field-pilot unit. The fourth year will concentrate on constructing and testing a field-pilot unit at a selected site and providing criteria for selecting the most appropriate NTP technology for DoD applications. The field-pilot reactor is meant to approach a practical scale device (flow rate in the Nm^3/hr range). In a practical application, for example, one would use several of these reactors in parallel to treat the exhaust gases from an emissions source.

The comparative assessment work will build upon a 1995 NIST workshop on NTP applications to air pollution control. NIST will also assist in plasma chemistry model development and laboratory measurements of reaction-chemistry relevant parameters (e.g., role of water-cluster reactions; DFWM-degenerate four wave mixing optical technique for in-situ measurement of species concentrations). Reactor performance measurements will be carried out at ARL using GC/MS (gas chromatography/mass spectrometry), TDL (tunable diode laser), and LIF (laser induced fluorescence) probes. ARL will also carry out CFD (computional fluid dynamics) calculations to predict and optimize fluid flow patterns and treatment residence times. Los Alamos will focus on electric discharge physics, electrical drive circuit engineering and optimization, and the design and construction of laboratory test, pilot and scaled-up reactors.

Earlier SERDP work, EQ work, and NIST collaboration feeds into this new project.

8. Expected Payoff:

Potential Users - Example, high-priority needs for three DoD service are listed below.
Air Force: 1) NOx (and potentially SOx) abatement in JETCs and CMTCs (Cruise Missile test cells) - a low back-pressure, filterless, scrubberless system is highly desirable, 2) NESHAPS-related emissions (e.g., metals in paint particles, dust).
Army: 1) Ordnance manufacturing and demilitarization emissions abatement; PEPs (propellants, explosives and pyrotechnics); 2) Reduction of heavy metals; 3) VOC emissions; 4) Zero-emissions fire extinguisher (Halon replacements) testing facilities.
Navy: 1) Abatement of HAPs (heavy metals) associated with metal cleaning and finishing; 2) NOx abatement for marine diesels and gas turbines; 2) Emissions abatement in ordnance manufacturing and demilitarization; 3) VOC emissions control in fuel storage and handling.

Impact - Regulations under the present Clean Air Act and expected future restrictions on Nox/HAPs/VOCs are presenting a major challenge to current emissions-control technology related to DoD and DOE emissions. NTP technology shows promise for addressing current and future needs, but the scaling and optimization of reactors is not well developed and criteria for selecting an appropriate technology are not available. This project is expected to demonstrate scaling and optimization and develop the needed selection criteria. Particular technical impacts are an increase in efficiency of electric-discharge NTP (by control of discharge physics and plasma of chemistry) and the potential for development of low back-pressure, filterless, scrubberless NOx control equipment from reductive mode processing (i.e., go to N_2 and O_2 terminal products), effected by improved electrical driver technology. Also, other VOC-abatement technologies have not yet been fully proven, so NTP is a back-up in some cases.

9. Milestones/Accomplishments:

1. Program Strat	11/20/95
2. Complete NTP technology assessment and discharge/e-beam white paper	02/28/96
3. Complete design and construction of lab-scale prototype reactors	06/30/96
4. Complete initial reactor performance and benchmarking measurements	09/30/96

In the future, we expect to evaluate and develop non-thermal plasma (NTP) reactor technology for the reduction of atmospheric emissions.

10. Transition Plan:

In this project, we expect to rigorously evaluate and demonstrate scaleable NTP technology through the field-pilot level and to establish DoD-relevant selection criteria. By applying engineering scale-up and selection criteria, a full-scale implementation can be made. Then, actual technology implementation at full-scale is envisioned to take place under collaborative industrial agreements for technology transfer.

11. Funding: $(K)

Performer	FY96	FY97	FY98	FY99
LANL	210	220	230	330
ARL	200	215	230	330
NIST	90	90	90	50
McMaster Univ		25	25	15
TOTAL	500	550	575	725

12. Performers:

Los Alamos National Laboratory (focus on discharge physics and prototype engineering) and the Army Research Laboratory (focus on CFD codes and reactor performance measurements) and the primary performers. The National Institute of Standards and Technology (NIST) will be a subcontracted performer for kinetics models and selected laboratory measurements. McMaster University (Prof. J.S. Chang) will be a subcontractor for consultation on reactor design, discharge physics, reaction chemistry, and hybrid reactors. Collaborations with the Lawrence Livermore National Laboratory (Dr. B. Penetrante), Tinker AFB, and McClellan AFB (through CH2M Hill and High Mesa Technologies LLC) are envisioned.

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14. Keywords:

Non-thermal plasma, oxides of nitrogen, hazardous air pollutants, volatile organic compounds, air pollution abatement, electrical discharges

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Reduction of NO_x Emissions from Marine Power Plants

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Surface Warfare Center (NSWC)

5. **Project ID:** #42

6. **Problem Statement:**

The California Air Resources Board (CARB) and the Environmental Protection Agency (EPA) have proposed limitations on the emissions of NO_x from ships passing through or operating within 100 nautical miles of the United States littoral by CY1995. Consequently, the Navy has been directed by OPNAVINST 5090.1A to make a good-faith attempt to comply with these limits on emissions in order to avoid costly fines and litigation.

At least 131 destroyer and frigate class ships employ gas-turbines plants, the LM2500, for propulsion, and many more also use the 501K gas turbine for power generation, representing an all-ship inventory of about 700 turbine units. These ships, returning periodically from remote tactical duty stations to replenish resources at home ports, pass through coastal waters within the 100-mile limit. The emissions from their power plants are presently in severe violation of the proposed NO_x limits for gas turbines.

Current state-of-the-art developments in low-emissions gas turbines are based on a dry low NO_x (DLN) combustor, and a water-injected low-NO_x combustor (which is similar in some aspects to the steam-injected combustor of General Electric's steam-injected gas turbine). Both are capable of reducing NO_x emissions below the anticipated CARB-mandated 42 volume ppm limit for gas turbines. Both combustors rely on a decrease in the average temperature of the flame zone to reduce the production of NO_x. (High temperature catalyzes the cleavage of the nitrogen molecule.) However, to cool the flame zone by air dilution, the size of the DLN combustor must increase substantially. To cool the flame zone with water, purified water normally available from the ship distillation plant, is required.

It is anticipated that for new construction, of the two technologies, the DLN combustor will have the least ship impact and cost. Nevertheless, the DLN spatial requirements reflect some uncertainty over whether the DLN system is subject to immediate retrofit without some rearrangement within the existing unmodified LM2500 enclosure. DNL combusters have been developed only for gaseous fuels. Liquid-fueled DNL combustors are under development. Modification to the component configuration within the enclosure to provide compatibility with the geometry and spatial requirements of a liquid-fueled DLN combustor appears necessary.

Based upon the fact that the General Electric Company already markets, for NO_x suppression in the existing engine a water-fuel manifold, the water-injected combustor (WIC) represents an inexpensive, low-risk alternative system, which is immediately amenable to retrofit in the LM2500 enclosure. Even if no problems are encountered in the DLN modifications, demonstration of a WIC system for NO_x reduction represents a prudent fallback development of a proven (in land-based plants), simpler, retrofit system.

Guiding principles expounded above for gas turbines are not universally applicable to diesel engines. For example, the DLN combustor approach would not be employed. Of the combustion-flame-cooling methods, water injection has been examined by many researchers in the academic and/or diesel contractor community with positive expectations that WIC methods may satisfy Navy needs for abatement of emissions in diesel plants. However, there will be a different retrofit response for ocean-going (such as the LST41 and some LCD-class ships) as opposed to harbor craft.

The task of assessing the ship impact of a WIC retrofit has been superficially examined with respect to water needs, and appear manageable. It is expected that a typical speed profile for a DDG-Class ship traversing the 100-mile coastal zone will operate about 70% of the time at 20 knots (cruise), 20% of the time at about 12 knots and 10% of the time at 5 knots. The total time will be under 5.92 hrs and the total fuel consumption will be 26.4 long tons (lt). The ships service generator is assumed to operate at 2500 kW with overall fuel consumption of 4.5 lt, or a total of 30.8 lt. Water requirements for the WIC system will be 31 lt at these conditions. Slower speed profiles will require less fuel, and therefore, less water.

A typical DDG is outfitted with two 12000-gal/day distillation plants. Each can produce 45 lt/day of water containing less than 1 ppm of total dissolved solids. Although General Electric has specified 0.1 ppm of total dissolved solids for continuous STIG engine operation (many thousands of hours per year), the total salt accumulation per gas turbine unit would be under 0.035 lbm during the few hours of traverse. Since salt is normally ingested via the input air and fuel streams, the LM2500 is washed down after 24 hrs of operation during regular service (this corresponds to washing down a unit every six days). Since a DDG will pass through a coastal zone once every six to twelve weeks, there will be about twelve additional washdowns per year.

Since the water purity level required for WIC-equipped diesel engines, is less exacting than the water purity level of gas turbines, potable water may be employed. Nevertheless, the diesel plants for seafaring ships will tap into the distilled water system in the same manner as proposed (vide infra) for the gas turbines. It is expected that port-bound boats will utilize a separate water storage tank, equal in capacity to that of the fuel tank, replenished along with fuel, from at-dock, potable-water resources.

The water storage capabilities of a DDG are 60 lt in four tanks. The anticipated operational procedure would dedicate the water of two of the four distilled water tanks (about 30 lt) for water injection of two LM2500 units (only two units are required to maintain cruise speed) during traverse of the coastal zone.

Engineering aspects of the fuel-injection system, the water system, the water feed manifold, monitoring systems for the NO_x, WIC system control, and shipboard testing need to be rigorously evaluated through analysis and operational investigation. Indeed, the aforementioned naval, at-sea, operating scenario for the reduction of NO_x has not been confirmed, either in simulation or test. The credibility of the water-injected combustor system, within the Navy community, as a viable alternative for acceptable NO_x reduction in the emissions of Navy gas turbines may be achieved only through a realistic shipboard evaluation.

7. Project Description:

The water-injected combustor approach to NO_x reduction in gas turbines will be evaluated in a shipboard configuration aboard a designated Navy destroyer or frigate on a routine mission.

The WIC-modified LM2500 (the 501K is not included in this project) gas turbine plant, and its components, the water-injected combustor, distillation plant, potable water storage tanks, an electronic feed control system, NO_x-monitoring equipment, and the impact of the WIC system on the ambient ship systems will be closely examined. The emission of NO_x from the gas turbine will be measured before entry into the coastal zone to establish a baseline reference condition. Measurements of the NO_x emissions will be automated to obtain a continuous record of emissions performance, which may ultimately be demanded by CARB. Real speed profiles will replicate the most likely naval experience.

The existing LM2500 combustors require orderly investigation of system hardware choices, system specification, and some fabrication of new components. Water feed will enter through the secondary row of fuel nozzles. Mixing and homogenization of water and fuel will be effected in a "tee" connection to the fuel manifold, which is adequate according to the manufacturer's (General Electric) experience.

Modification of water, and fuel feed pumps, and the electronic feed-control system (contractor supplied) will ensure conformity with the constraints of the gas turbine container and the ambient ship environment.

Modification of shipboard diesel engines for water injection will be explored at land-based facilities, in conjunction with contractors, who have already faced the problems of fuel-injector erosion and corrosion. The method of mixing the fuel will be investigated to avoid the unpredictable effects of slug flow, flame quenching, with consequent "missing" of cylinders, and loss of power. Fuel-water emulsion may be essential for predictable performance. Methods of facilitating the emulsification process with detergents must be examined. The corrosive effects of detergents on the structural metals must be closely observed. Testing of diesel fuel injector configurations will take place largely in shoreside facilities pending successful resolution of fuel injector studies and tests.

Distilled water from the distillation plant will be manifolded to the potable water tanks with new valve controls dedicated to priority delivery of the distillate to new water-feed pumps during passage through the coastal zone. However, tests of the WIC system will be undertaken during

regular cruise conditions with the permission of NAVSURFLANT and the ship commander.

Following each traverse of the coastal zone (and any other test), a washdown, examination, and a close analysis of the combustor for corrosion damage will occur. Corrosion could develop in the combustors of gas turbines, should the combustor be exposed to continuous, long-time, high levels of sodium exceeding 0.3 ppm of water, reduce the life of the engine, and invalidate the manufacturer's guarantees. Corrosion could limit the efficiency of fuel injectors in diesel engines with similar negative effects on guaranties.

The ship impact and influence factor of each element of the WIC system will be measured, in order to permit design of a fix should any problems arise.

The project will provide data on the performance of the WIC system with respect to reduction of emissions and efficiency during anticipated realistic operations. The alternative NO_x-reduction methods will be assessed, because the scrubbing approach to diesel emissions will be proceeding simultaneously. The delivered products will include a credible statement of WIC characteristics, and a relative cost assessment of the alternative NO_x reduction systems. Based upon these experimental test data, and the relative cost estimates, a set of management recommendations will be offered to the Navy.

This project is in support of the Compliance Pillar in the Tri-Service Environmental R&D Strategic Plan.

8. Expected Payoff:

This project provides the Navy with a less risky, competitive, alternative retrofit of existing engines complying with EPA and CARB-proposed operational limits on the emission of NO_x from ship gas turbine power plants during traverse of the coastal zone. It will deliver data on the operational characteristics and relative merits of the water-injected combustor system for gas turbines, and fuel-plus-water injectors for diesels, providing reasonable bases for critical decisions necessary for complying with the CARB mandates.

9. Milestones/Accomplishments:

1. Develop Joint Navy-Contractor Strategy	10/94
2. Commit the Navy to a Test Ship and Test Engine	10/94
3. Identify Long Lead-Time Components and Systems	12/94
4. Design Test Components and Test Monitoring Systems	03/95
5. Modify Diesel Engine Fuel-Injectors	03/95
6. LM2500 water-injection with manual water control	05/95
7. Water manifold and controller procurements	08/95
8. Engineering assessment of alternative NOx reduction methods for diesels	05/95
9. Complete component Procurement Process	07/95
10. Assemble Land-Based Systems (Turbine & Diesel)	09/96
11. Test the Land-Based Systems	03/96

12. Management Review and Go/No-Go Decision	05/97
13. Modify the Test Ship Turbines for Water Injection	07/97
14. Start Shipboard Tests	10/97
15. Complete Shipboard Tests	01/98
16. Report, Assessment and Management Review	04/98

Testing of water-fog injection into the compressor bellmouth of the LM2500 to suppress NO_x emission was completed in January. The tests demonstrated that water-fog injection reduces NO_x emissions without the loss of thermodynamic efficiency. However, since water-fog injection at the bellmouth requires significantly more water than water injection into the combuster, this method will not be pursued. Nevertheless, at the management review of water-fog injection, it was concluded that water-fog injection into the bellmouth may realize an increase both in thermodynamic efficiency and output power at modest cost. A proposal to develop this concept has been approved by Mr. Daniel A. Groghan, NAVSEA Code 03X3, and presented to Mr. Wayne W. Bobbitt, Code 827, for transmittal to 6.2-level money manager, Mr. James A. Gagorik, ONR Code 334.

The existing (simplex) fuel manifold of one LM2500 gas turbine of the ship engine simulation facility was modified to accept a manually controlled water-feed system. The simplex manifold will undergo tests to determine whether it can accept sufficient water to suppress NO_x emission CARB-proposed limits. Since the tests have been positive, the cost of retrofitting Navy LM2500 gas turbines may fall substantially (the cost of the duplex manifold is about $100K without installation).

The Covington Detroit Diesel Company delivered a DDC Model 4-71 two-stroke engine to the EPA site at Research Triangle Park, NC. This engine permits testing of two alternative approaches to NO_x reduction in diesels. Accurex, the EPA contractor, is assessing the economical viability and Navy ship impact of water injection versus the exhaust-gas recirculation system for the suppression of No_x emissions from diesel engines.

10. Transition Plan:

Discussions with Contractor (Seaworthy Systems Inc., General Electric Co., Allison Gas Turbine Co. and Detroit Diesel Co.) principals have been underway to determine whether the milestone schedule is not too compact. There is a verbal agreement over the participation of the Contractor and the forms of cooperation needed to facilitate the project.

The project will ultimately go forward to retrofit-system specification and fleet procurement of retrofit hardware for the water-injected gas turbines, and to recommendation of diesel modifications and a set of system layouts for Navy harbor craft.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	Total
SERDP	750	300	1,000	850	500	3,300
EPA	250	250	50	50	0	600
Total	1,000	550	2,000	900	500	3,900

12. Performers:

Participants in the study include CDNSWC, U.S. EPA, APPCD, the Norfolk Naval Shipyard, and contractors. Program management, development facilities, land-based LM2500 and 501K test engines, a Navy diesel test engine, distilled water system components, and NO_x-monitoring systems will be supplied by the CDNSWC. Water feed manifold(s), manifold interconnections, and the electronic water and fuel control system will be provided by the Contractor(s). Installation of shipboard gas turbine manifolds, and water manifolds will be performed by the Norfolk Naval Shipyard. NAVSURFLANT will designate a test ship for evaluation.

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14. Keywords:

Gas Turbine, Diesels, NO_x Emissions, Water injection

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Lead-Based Paint Hazard Mitigation

3. **Agency:** U.S. Army Corps of Engineers

4. **Laboratory:** Construction Engineering Research Laboratories (USACERL)

5. **Project ID:** #521

6. **Problem Statement:**

This SERDP project addresses needs documented in Tri-Service Environmental Quality Strategic Plan (Green Book) Requirement Thrust 2.L.5a: Satisfy RCRA (Treatment/disposal of Operations Waste). Furthermore, this work addresses high priority Army-wide Requirement Statements: Compliance 2.3.k Lead-Based Paint Testing/Disposal; Compliance 2.5.a Lead-Based Paint Removal; Compliance 2.6.a Find Abrasive Substitutes for Removing Paint; and Pollution Prevention 3.2.c. Cost Effective Lead-Based Paint Abatement.

The DoD wide lead-based paint (LBP) hazard mitigation cost has been estimated to be more than $1 billion over the next 10 years. The increased cost for LBP abatement is due to the additional requirements for containment of dust, environmental monitoring, worker protection, and disposal of hazardous waste. Human exposure to lead is associated with adverse health effects, including permanent damage to the central nervous system. About 75% of all homes constructed in the United States before 1978 have some LBP. While many sources of lead exposure exist, lead from lead-based paint is the most significant source of exposure at DoD installations. Although lead is no longer used in house paints and the application of lead primers on steel structures is declining, old paints with hazardous levels of lead remain on many surfaces today. Traditional methods of paint removal, such as abrasive blasting, or chemical stripping, can be used to remove LBP. However, the costs of containment, worker protection, and waste disposal make many of these traditional methods cost prohibitive where the paint contains lead. The overall goal of this project is to develop improved methods for LBP hazard mitigation to reduce costs and enable compliance. The majority of the work in this project falls under Applied Research/Technology Demonstration (6.2/6.3a).

7. **Project Description:**

This is an integrated multi-disciplinary, multi-agency project. The technical objectives of this project are (a) to develop novel vitrification technology for lead-based paint removal that can be used effectively for immobilization of heavy metal hazardous waste (b) to evaluate the use of new abrasive sponge blasting media for lead-based paint removal (c) to develop a microwave

assisted robotics system for removal of lead-based paint and (d) to develop and demonstrate an integrated "Lead Hazard Mitigation and Management System (LMS)". Objective (a) will minimize the amount of hazardous waste produced during LBP removal. Objectives (b) and (c) focus on environmental compliance and improving worker and public safety. Finally, objective (d) will assist installations in developing the most cost effective LBP hazard mitigation strategy. The technical approach for this project will be phased to include the following:

a. Glassy Materials Modeling for Hazardous Waste Immobilization

The Resource Conservation and Recovery Act (RCRA) mandated Land Ban requires that hazardous waste be treated to below the characteristic level prior to disposal. Heavy metal hazardous waste residues have been effectively vitrified in the matrix of glassy materials. The actual mechanisms by which these materials are immobilized have not yet been determined. Laboratory experiments have determined that bonds within the glass network break, providing bonding sites within this network for the heavy metal cations. Similarly, the cations may become part of the lattice structure by randomly occupying interstitial and/or defect sites. The long term durability of the vitrified and cement stabilized waste forms needs to be evaluated so that the leaching behavior of materials under actual field conditions can be modeled and predicted.

The technical approach will involve the development of a glass composition to vitrify materials containing heavy metal hazardous waste and determining through characterization techniques such as.X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM), how the hazardous waste is incorporated within the glass structure and immobilized. The mechanisms of the vitrification and ion leaching processes will be modeled to optimize hazardous waste immobilization. One application process, is to thermally spray a molten glass compound directly onto a lead containing substrate. This has shown the potential to effectively contain the hazardous waste residues without producing lead dust or airborne lead. Thermal energy to melt the glass can also be applied by microwaves using susceptor materials such as graphite. The mechanism by which heavy metals become immobilized will be investigated. Existing and recently developed laboratory tests will be used to predict the long term durability of the vitrified waste form.

b. Sponge Blasting

USACERL is evaluating emerging technologies for the removal of lead-based paint from DoD buildings and structures. The technologies being evaluated include cryogenic blasting, laser paint removal, chemical stabilizers, alternate chemical strippers, and confined hydraulic blasting. The sponge media blasting technique appears to be particularly promising for LBP removal from surfaces of buildings. Soft sponge media abrasive products have been developed to address issues of worker and public safety, hazardous waste minimization, and pollution prevention. The sponge media consists of a matrix of water-based urethane foam within which the abrasive particles are dispersed. The media can be wet with water or chemical solutions to increase productivity. The aggressiveness of the sponge media can be tailored for the specific application by changing the characteristics of the abrasive particles inside the urethane foam. During field

testing, it was determined that sponge blasting caused unacceptable damage to historical wooden structures.

For the field demonstration of emerging LBP technologies, sites will be selected from typical building surfaces. Pre-abatement testing of the structures will be done to characterize the painted surface, including paint thickness, type, and uniformity. Post-abatement tests will be done to determine how efficiently the process works from the viewpoint of completeness of the lead removal. Hazardous wastes will be carefully contained, collected, tested, and disposed. Cost data will be recorded for all work phases and the performance envelope will be validated.

c. Microwave Assisted Robotics Paint Removal System

USACERL has invented and patented a process to remove lead-based paint using microwave coupling compounds to provide the heat. In this process a slurry of microwave enhancers such as graphite mixed with powdered glass is applied to the wooden structure which is then exposed to microwave energy. The heat produced by microwaves softens the paint which can be removed easily. A field usable microwave applicator integrated with sensors and a robotic manipulator needs to be developed. Robotics technology is particularly well suited for simple, repetitive tasks such as paint removal. A practical microwave assisted robotics paint removal system will be assembled, resulting in low cost, environmentally safe LBP removal. The mobile robotics platform will be equipped with necessary sensors. After laboratory evaluation, the microwave assisted robotics paint removal system will be field tested at DoD installations to establish the technical validity and cost-effectiveness.

d. Lead Hazard Mitigation Management System (LMS)

A Lead Hazard Mitigation Management System (LMS) will be developed to assist engineers in developing the best LBP abatement strategy for their specific installation. The system will provide assistance with (1) installation-wide prioritization of abatement projects, and (2) selection of the best abatement method for a given situation. User inputs to LMS will include (1) a structure inventory which catalogs background information such as substrate type, building use, and age, and (2) field test information such as identification of potential lead-based paint hazards, lead testing results, and coating condition index. The knowledge base will be able to be updated as new hazard assessment and abatement technologies emerge or as regulations change. The technical approach will include development of information and procedures required for decision making; development of the coating condition index; development of the knowledge bases; development of methodologies and decision trees for prioritization and alternative selection.

Key technology barriers in this project which need to be overcome are: prediction of the long term durability of the vitrified glass and other stabilized waste forms, optimized formulation of urethane foam abrasives, and integration of microwave applicator and sensor systems. The proposed research has many innovative and novel aspects and therefore, the probability of overcoming these barriers is high. This project has a low risk and high payoff.

8. Expected Payoff:

The urgency of the lead-based paint problem has increased due to the Base Realignment and Closure Act, where the installations are required to abate their residential buildings of lead-based paint. The DoD wide cost of lead-based paint hazard mitigation is estimated to be more than $1 billion, therefore it is imperative that effective decision making tools be utilized to ensure that the most cost effective, environmentally safe project plans are developed using emerging technologies. The proposed lead paint removal technologies combine the advantages of vitrification with microwaves. Use of the LMS integrated hazard abatement strategy will allow full consideration of appropriate abatement technologies based on the coating condition index. If we assume 10% reduction in the cost of lead-based paint abatement, then the return on investment is approximately 25:1. The ultimate payoff is that this project would provide valuable assistance to insure that a DoD installation is not in violation of regulatory requirements for lead-based paint hazard mitigation, as well as provide healthier homes to military service members and their families.

9. Milestones/Accomplishments:

		Planned	Completed
1.	Prepare vitrified materials	06/94	06/94
2.	Complete lab study of glass processing parameters	03/95	03/95
3.	Complete glass microstructure investigation	09/95	07/95
4.	Complete evaluation of sponge media	06/95	
5.	Complete glassy materials development	07/96	
6.	Develop the alpha version of LMS	10/97	
7.	Complete microwave system prototype test	12/97	
8.	Complete field tests and demonstrations	04/98	
9.	Complete reports and technology transfer documents	09/98	

A new thermal spray vitrification (TSV) process to remove lead-based paint from steel, masonry and concrete structures was invented and patented. A designer glass composition containing silicon dioxide, boron oxide, iron oxide, lithium oxide, sodium monoxide, aluminum oxide and other oxides was developed to immobilize hazardous metals such as lead, chrome and cadmium in the glass matrix. Another process to remove lead-based paint from wooden structures using microwave coupling compounds such as graphite was invented and patented. The in situ vitrification and paint removal processes when commercialized will reduce the cost of lead-based paint removal by a factor of two.

A paper titled "Vitrification of Lead Contained in Lead Based Organic Coatings Using Thermal Spray Technology" was presented at the ASTM sponsored Third International Symposium on Stabilization/Solidification of Hazardous, Radioactive, and Mixed Waste, held in Williamsburg, VA, 1 November 1993. A paper titled "In Situ Vitrification and Removal of Lead-Based Paint for Steel Structures" was presented and published in the Proceedings of the 8th. National Thermal Spray Conference, 11-15 September 1995, Houston, TX. Two U.S. Patents (5,268,548 and 5,292,375) titled "Microwave Assisted Paint Stripping" and "Removal of Lead Based Coating by Vitrification" were granted in 1994. Another U.S. Patent application titled "Vitrification and

Removal of Coatings Containing Hazardous Materials" was filed in 1996.

10. Transition Plan:

Field tests and demonstrations of vitrification and sponge blasting will be conducted at DoD installations. LMS will be implemented at a DoD installation to provide hazard assessment and the optimized mitigation strategy. In order to transfer the methods and technologies developed in this program an intense documentation effort will be required and full coordination will be achieved through the "DoD Interagency Lead-Based Paint Task Force". Tri-service guidance documents including Engineering Technical Letters, Guide Specifications, User Guides, and Technical Manuals will be prepared for the use of DoD installations. The thermal spray vitrification (TSV) process will be tested and validated, using ESTCP funds in FY96, for application to DoD steel structures such as ships, bridges and hangars. The Army patents on vitrification and removal of lead-based paint will be licensed and commercialized.

The technologies developed and demonstrated under this SERDP project have dual use application in the Department of Housing and Urban Development (HUD) and Department of Transportation (DOT).

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	FY98
SERDP	700	400	700	600	750

12. Performers:

U.S. Army Construction Engineering Research Laboratories, Champaign, Illinois, will be the lead laboratory. Other performers in this project are the U.S. Environmental Protection Agency, National Risk Management Research Laboratory (POC: Mr. John Martin); and DOE Savannah River Technology Center (POC: Dr. James Marra). Academic involvement includes but is not limited to University of Illinois. The work in this project has a high potential for a CRADA with the industry.

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14. Keywords:

Vitrification, Leaching, Modeling, Hazardous, Microwave, Lead Abatement

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Emission Reduction Planning Model

3. **Agency:** U.S. Air Force

4. **Laboratory:** Armstrong Laboratory (AL)

5. **Project ID:** #175

6. **Problem Statement:**

The 1990 Clean Air Act Amendments (CAAA-90), the first major revisions to federal air legislation since 1977, mandate a substantially more complex air pollution compliance program. Title III (Air Toxics Provisions) and Title V (Permit Provisions) of the CAAA-90 present especially difficult, long-term compliance challenges for Department of Defense (DoD) installations. Although air pollution programs at DoD facilities are similar in that they consider similar sources, the program at any site must consider specific local conditions. These conditions include the number and type of air pollution sources, operation and maintenance activities, the facility's mission, and the regulatory environment to include both regional and local concerns. Prevention, minimization, and control of pollution, as well as administrative management, are all components of an optimal, cost-effective compliance strategy. Development of a compliance strategy can become overwhelming for DoD environmental personnel at the base level due to the complexity of the problem and possible solution approaches. Poorly planned compliance strategies can lead to (i) non-compliance with air pollution regulations, (ii) mission impairment from regulatory action (notice of violation, fine, activity limitation, shutdown), or (iii) excessively expensive or inappropriate solutions. Conversely, well-planned, cost-effective compliance strategies will avoid compliance problems, leading to enhanced relationships with regulatory agencies and surrounding communities, as well as reducing air pollution.

Previous funding for the Emission Reduction Planning Model (ERPM) has led to the development of a prototype decision support system. A full-scale decision support system for establishing and maintaining optimal, cost-effective compliance strategies would greatly aid environmental personnel in developing appropriate compliance strategies. Funds are requested to expand an existing joint Air Force/Army/EPA applied research initiative and to support the demonstration of the ERPM at several federal facilities.

7. **Project Description:**

a. Technical Objective: The objective of this project is to develop a state-of-the-art decision support system to aid environmental personnel in reducing air pollution compliance problems. The availability of such a system will allow for consistent, optimal, and cost-effective application of control technologies, prevention measures, and mitigation techniques. The proposed decision

support system is intended to support, not replace, experienced environmental personnel.

b. Technical Approach: To date, the ERPM research program has resulted in the development of a prototype decision support system. The prototype system tested assumptions on how to encode facts, relationships, and inference methods required to develop air pollution compliance strategies. The prototype system, while small in scale, has demonstrated that a decision support system of this type is feasible and potentially very useful for developing compliance strategies.

The full-scale decision support system will follow design and function of the prototype system. Algorithms based upon EPA, DOE, and DoD expertise will be constructed to assess current base emissions, applicable regulations, available control devices, and compliance alternatives (i.e., pollution prevention, pollution minimization, and administrative techniques) in order to recommend prioritized actions that optimize regulatory, economic, and environmental benefits. Draft software packages will be user tested at selected Air Force and Army installations to gain insight for improving system utility and ease of operation.

c. Technical Challenges: The primary technical challenge will be integrating expert system algorithms with external databases and pre-existing models. Secondary challenges include obtaining acceptable execution times on a user-friendly software platform.

d. Tasks: Phase I of the project will include the incorporation of control technologies and federal regulations into the decision support system as well as the development of an interface with existing emission inventory databases and dispersion screening models. Phase I will be completed with an in-house review of work to that point and a field demonstration of the phase I decision support system.

Incorporating control technologies into the decision support system involves a survey of the state-of-the-art control devices. Both criteria pollutants and air toxics will be considered for each source category as control devices often affect more than one pollutant. A broad spectrum of alternatives will be considered so that the most cost-effective and environmentally acceptable approaches are identified. As each of the various control devices for each source category are specified, the corresponding expert-system rules will be written and implemented in the decision support system.

Incorporating applicable federal regulations into the decision support system involves a survey of the regulations that apply to various sources present at federal facilities. As regulations are identified, the expert-system rules associated with these regulations will be developed and implemented into the decision support system.

Development of an interface with existing emission inventory database systems (e.g., AQUIS, APES, etc.) will allow the decision support system to take advantage of the vast number of source and emissions data that are available in emission inventory databases. The interfaces will prevent the duplication of functions already performed by emission inventory database systems such as estimating emissions.

Developing an interface with dispersion screening models will provide a link between source emissions and regulations based on ambient air quality standards. The screening technique will provide a conservative estimate as to whether a source is out of compliance with ambient air quality standards, as well as to determine if a proposed control technology's efficiency will be sufficient to meet an applicable ambient standard.

Phase II of the project will include the incorporation of compliance strategies beyond control technologies into the decision support system, and the development of an interface with advanced EPA-approved dispersion models.

Phase II will be completed with a field demonstration of the entire decision support system. Once the phase II field demonstration is complete, modifications to the decision support system will be affected and the final software package, documentation and report will be prepared.

Incorporating compliance strategies beyond control technologies involves a survey of pollution prevention, pollution minimization, and administrative management techniques that are applicable to DoD facilities. Optimal, cost-effective and environmentally acceptable compliance strategies can only be developed when considering this complete range of compliance methods. As each of the various compliance strategies for each source category is specified, the corresponding expert-system rules will be written and implemented in the decision support system.

Developing an interface with advanced EPA-approved dispersion models will provide a link between source emissions and regulations based on ambient air quality standards. The incorporation of dispersion modeling capability will provide a more accurate estimate as to whether a source is out of compliance with ambient air quality standards, as well as to determine if a proposed compliance strategy will be sufficient to meet an applicable ambient standard.

e. Relationship to DoD Environmental Objectives: This project directly supports Tri-Service Environmental Quality Strategic Plan requirements 2.I.2.e, DoD-Wide Emission Management System and Database, and 2.I.2.k, Assess Atmospheric Impact of Air Base and Aircraft Operations for Compliance with CAA and for EIAP.

8. Expected Payoff:

This project will ultimately provide a state-of-the-art decision support system to aid environmental personnel in determining areas of potential violations and compliance options, thus leading to installation-specific, cost-effective air pollution compliance strategies. Moreover, DoD-wide use of the decision support system will provide consistency in the treatment of air pollution problems. The decision support system will be designed to easily adapt to other industries as well as to the needs of local, state, and federal regulatory agencies. Further, incorporating EPA-approved methodologies in the decision support system will help to expedite the regulatory acceptance of a facility's compliance strategy. Finally, the design of the decision support system allows for its application many years into the future, and easy integration of new compliance strategies and regulations.

9. Milestones/Accomplishments:

1. Complete control technology database	05/95
2. Complete federal emissions standards	07/95
3. Complete phase I testing of software	09/95
4. Complete data extraction from existing emissions inventory database	09/95
5. Complete interface with emission inventory database	02/96
6. Modify code per Phase I feedback	04/96
7. Complete dispersion screening model	07/95
8. Complete Phase II field demonstrations	02/97
9. Modify per Phase II feedback	05/97
10. Completed software/documentations/final report	09/97

To date the control technology database and federal admission standards have been accomplished. The phase I testing of the software has been completed and complete data extraction from existing inventories has occurred.

10. Transition Plan:

The resultant decision support system will be implemented at Air Force and Army installations throughout the United States via the Air Force Center for Environmental Excellence (AFCEE) and Army Environmental Center (AEC), respectively, as well as potential application by DOE and other federal agencies. Further, there exists significant potential for EPA adoption as an accepted and encouraged means of compliance evaluation and planning.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	200	100	200	400	900
Air Force S&T	201	0	0	0	373
Army S&T	190	205	0	0	470
EPA	0	0	0	0	15
Total Project	591	505	400	400	1,758

12. Performers:

The Environics Directorate of Armstrong Laboratory (AL/EQ)will coordinate this development effort with the Army's Construction Engineering Research Laboratories, Department of Energy's Argonne National Laboratory, and the Environmental Protection Agency's Air and Energy Engineering Research Laboratory.

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14. Keywords:

Air Pollution, Compliance, Planning, Emissions, Controls, Model.

SERDP FY96 PROJECT DESCRIPTION

1. SERDP Thrust Area: Compliance

2. Title: Laser Ablation/Ionization Characterization of solids

3. Agency: Department of Energy

4. Laboratory: Pacific Northwest National Laboratory

5. Project ID: #362

6. Problem Statement:

The Department of Energy (DOE) is currently undertaking the enormous task of remediating defense wastes and environmental insults which have occurred over 50 years of weapons production. It is abundantly clear that significant technology advances are needed to characterize, process, and store highly radioactive waste and to remediate contaminated zones. Aside from the processing and waste form issues, analytical technologies needed for the characterization of solids, and for monitoring storage tanks and contaminated sites do not exist or are currently labor-intensive tasks. The purpose of this research is to develop widely applicable mass spectrometry techniques for analysis of mixed chemical wastes. The sensitive and rapid analysis of,organics, inorganics, and TRU's in contaminated soils, groundwater, and in tank wastes is a key Hanford-site need. The urgent need for this work has been highlighted by recent findings of the DNFSB, and by the agreement between the DOE, EPA, and Washington State.

The remediation of Hanford-site defense waste and the long-term disposal of high-level mixed wastes requires chemical analysis of the waste streams. The projected costs of these tasks, with current methods, is in excess of $500M. Analysis of mixed waste is needed to characterize the chemical classes and concentrations of a wide variety of waste materials. Tank and crib waste sites contain broad distributions of both organic compounds; aromatics, nitrates, chelating agents, and halogenated hydrocarbons, and inorganic compounds chromates, ferrocyanides, metals, and TRU's. The chemical speciation and concentration of these materials must be determined in order to design effective clean-up strategies. Additionally, the high concentrations of radioactive waste materials, in tanks and cribs, provide an energetic driving force that continuously transforms mixed waste in complex kinetic pathways. Hence, analyses need to be made in a timely fashion. Current methods require as much as six months for a single waste tank core sample analysis and report. Initial research will develop rapid laser-based analysis techniques, the principles of which may be extended to on-line field measurements.

This research impacts needs in both basic and applied research categories and will help determine the design parameters and evolution of field analytical platforms. The hot cell and field instruments being developed under the DOE/Hanford Mobile Analytical Reconnaissance System (MARS) program, as a part of the Hanford-site characterization program, constitutes a major effort in meeting remote analytical and characterization needs. This research is currently

operating under SERDP FY 95 funds as part of an ongoing program conducting fundamental studies in support of the Hanford-site characterization and MARS programs. Significant progress has occurred in the previous FY. This includes the modification of the ultra-high-vacuum laser ablation chamber, experiments on laser ablation of simulated tank wastes, and the development and demonstration of frequency-doubled diode laser technology for ultrasensitive resonance ionization detection.

For certain critical trace elements, it is important to focus on the method of ionization of the ablated material. Technitium-99 has been identified as a significant ground water contaminant at a number of locations on the Hanford Site. Because of its long half-life (214,000 years), high fission yield, and high rate of mobility in the subsurface, Technetium-99 is considered a hazardous radioisotope waste. Furthermore, Technetium-99 can be used as a critical path isotope for performance assessment of nuclear waste isolation barriers. Because Tc-99 is a long-lived pure beta-emitter, routinely available radiochemical- counting methods do not provide adequate sensitivity for use of Tc-99 as a performance assessment tool. However, the long half-life of Tc-99 does make it an ideal case for high-sensitivity detection by laser resonance ionization methods, which are responsive to the quantity of atoms present rather than the radioactive decay rate. Recent work has demonstrated that multiple-resonance laser induced ionization techniques can be successfully applied to the measurement of Tc-99 in environmental samples. The capabilities for detection of technitium have advanced in that a large number of possible excitation schemes have been investigated to optimize the overall efficiency and to suppress unwanted non-resonant ionization of other species. To date, the best excitation scheme involves a three step (3 laser) excitation into an autoionizing state using wavelengths of 313.2, 821.1, and 670.7 nm. Current investigations are designed to determine optimal excitation schemes, using resonances that overlap the emission wavelengths of reliable diode and titanium sapphire laser sources. Improvements on this methodology, are expected to ultimately result in a field-portable, routine analytical technology capable of rapid, accurate and sensitive measurements.

The major objectives of this research are:

1) To develop general and sensitive techniques for determining the molecular speciation of organics and inorganics in tank wastes and those chemisorbed on mineral soil substrates. These methods must be sensitive to a broad spectrum of compounds to detect the many species present in mixed waste environments.

2) To develop new methods for the detection of technetium. Development of multiphoton-ionization techniques is required to satisfy the critical need for sensitive and rapid detection of Tc-99 and Strontium-90. Current methods require weeks, laser analysis can be completed in hours.

3) To transfer this new knowledge to other applied DOE analytical programs such as the Hanford-site characterization and MARS programs.

7. Project Description:

Laser-based analysis techniques are proposed to achieve these goals, primarily laser ablation mass spectroscopy (LAMS) and resonance enhanced multiple photon ionization (REMPI). Laser ablation can vaporize nearly any solid material in pulsed plumes of sufficient concentration for detailed analysis by mass spectrometry, laser-induced fluorescence, and other techniques. The LAMS approach couples laser vaporization with ultrasensitive mass spectrometry. Analysis of even complex, multicomponent mixtures can be performed rapidly and requires very little sample. This is highly desirable for the analysis of many environmental samples and hazardous wastes. When the concentrated laser ablation pulses are combined with multiphoton ionization time-of-flight mass spectroscopy, the result is a versatile and sensitive analysis technique of very high mass resolution. The excellent mass resolution provides superb differentiation between compounds of similar masses and between isotopes. In addition, the resonant ionization process can provide excellent spectral resolution which extends and compliments the mass resolution. These features are crucial for the successful chemical speciation of complex waste samples.

The advantages of the LAMS approach include: Small sample requirements, minimum sample preprocessing, minimum waste generation, and reliable technology. However, several uncertainties are introduced by the ablation process. For instance, it is not clear how well the composition of the ablated (gaseous) products reflects the sample composition; some sample components can be preferentially ablated. Changes in the chemical state (e.g., changes in the oxidation state of metals) in the solid and gas phase are also potential problems. We propose to use several concurrent approaches to determine in more detail the mechanisms and consequences of laser ablation on model samples of simulated waste, and on relevant wide band gap inorganic materials, with and without chemisorbed species. Of particular importance are the effects of the ablation process, the defect-mediated coupling of light into the solid, the mechanism of particle emission, and particle interactions after emission but prior to the actual analysis. The analysis of organic species chemisorbed on mineral substrates is an extremely import application of laser analysis techniques due to the need to detect toxic wastes contained in soils for waste characterization and environmental compliance. Many organic waste compounds absorb strongly in the UV (e.g., trimethylamine, benzene, naphthalene, toluene, phenol, and chlorinated aromatics) and may prove especially amenable to laser techniques. The mechanisms of desorption and ionization of such molecules on macroscopic single crystals of MgO, quartz, NaNO3, and CaCO3 would also aid analysis. Developing quantitative analytical methods requires the study of both neutral and ionic species desorbed from the surface, their kinetic energies, and possible electronic excitations (gas phase luminescence studies) as a function of laser fluence and wavelength.

Technitium and strontium measurement systems to be addressed by this project will expand upon existing expertise and technology that has been developed at Pacific Northwest National Laboratory (PNNL). Resonance enhanced multiphoton ionization, coupled with mass spectrometry, has been shown to be an extremely sensitive and selective approach to the analysis of rare isotopes. This work at PNL has emphasized the use of high-resolution continuous-wave lasers to simultaneously maximize isotopic selectivity and absolute sensitivity, and has demonstrated detection limits in the attogram (10-18 g) range and the ability to detect a target

isotope in the presence of a 1010 or greater excess of other isotopes of the same element. Applying these methods to the measurement of Tc-99 and Sr-90 will involve collaboration with B. A. Bushaw to facilitate the rapid develop of specific excitation schemes and measurement procedures that can be addressed with compact solid state laser systems. Solid state laser technology has the advantage that it is reliable and easily incorporated into field analytical instrumentation.

8. Expected Payoff:

These programs will increase our capabilities to analyze mixed waste and detect technetium. The results will be useful in performing the analysis of tank and crib wastes and contaminated soils and groundwater. The near real-time analysis capabilities of these methods will also be important for monitoring waste retrieval, facilities decontamination, and other site restoration actions. It will contribute to the success of the Hanford-site characterization and MARS programs which is predicted to result in a savings of $30-75M during the first three years following its implementation. Similar percentage savings can be expected at other DoD and DOE sites.

9. Milestones/Accomplishments:

1.	Modify time-of-flight apparatus for rapid sample exchange	12/95
2.	Develop a cw diode laser scheme for excitation of Strontium and Calcium	12/95
3.	Determine matrix effects on ablation of waste compound EDTA and HEDTA	02/96
4.	Determine ablation/ionization efficiency using picosecond laser source	04/96
5.	Report results to MARS Program	09/96
6.	Calibrate ablation yield of waste compounds oxalic and citric acids, TBP, and sulfate	02/97
7.	Evaluate laser ablation for contaminated soil analysis	05/97
8.	Final report	09/97

The modified time-of-flight apparatus has been used to characterize known waste compounds such as EDTA (ethylene-diamine-tetra-acetic acid) sodium -nitrate, - phosphate, and -sulfate and waste simulant. We have evaluated the laser ablation to complex waste simulant using LAMS and calibrated several individual waste compounds. Ongoing studies indicate that matrix assisted laser desorption ionization (MALDI) will be very valuable for waste analysis as excellent speciation of EDTA has been achieved using this technique. The diode laser scheme for excitation of technetium has been designed and a diode laser-based resonance ionization experiment has been completed demonstrating ultrasensitive detection of calcium isotopes. The diode laser experiment may be extended to field detection of technetium and other important radioisotopes and as such represents a major success for our SERDP task. The optimal laser-ionization frequency and pulse duration has been determined for detection of molecular species in the UV region between 50,000 and 37,600 wavenumbers (cm-1). In particular, specific ionization schemes for desorbed species NO and CO have been determined. Laser pulse durations of 10 ns, 5 ns and 60 ps have been investigated for LAMS of nitrate waste compounds. A report of interim results for dissemination to applied DOE analytical programs such as MARS is in preparation.

Between May 21-27, 1995 one of the PI's (W. Hess) attended the Third International Conference on Laser Ablation (COLA) in Strasbourg France. COLA'95 was held in conjunction with the European Materials Research Society Meeting and constituted the largest symposium (over 195 contributed papers) within that meeting. Hess made an oral presentation of the paper entitled "Laser Ablation of Sodium Nitrate: NO Desorption Following Excitation of the p-p* Band of the Nitrate Anion" by W. P. Hess, K. A. H. German, R. A. Bradley, and M. I. McCarthy. This paper is to be published in the refereed Journal of Applied Surface Science and in the book of the conference proceedings. The paper was well received and initiated many conversations with other conference participants. To date, 10 publications have resulted from SERDP funding of this task (8 journal and two conference proceedings).

10. Transition Plan:

Key to the impact of this project is the teaming of the end user (WHC and PNNL staff from the Hanford-site characterization, MARS and related programs), and the SERDP scientific staff. The MARS team provides the engineering staff who have extensive experience in the development and delivery of highly technical, on-line, field and mobile instrumentation for the DOE and DoD. They are also indirect contact with potential industrial partners for the eventual production of instrumentation at Hanford and other federal facilities. Through this approach the findings of the SERDP program will be readily available to the end users.

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	TOTAL
SERDP	380	100	310	340	1,130
DOE	425	425	425	0	1,275
Total	805	525	735	340	2,205

*MARS related technology development program.

12. Performers:

The organizations performing the work are: The Department of Energy, Division of Basic Energy Research, and Pacific Northwest National Laboratory operated by Battelle Memorial Institute. A major beneficiary is the DOE MARS Program managed by PNNL for the DOE.

13. Principal Investigators:

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14. Keywords:

Mixed-waste, Analysis, Laser-ablation, Ionization, Characterization, Technitium.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Vapor Permeation VOC Recovery from Refueling and Storage (VOC Control Fueling/Fuel Storage Operations)

3. **Agency:** U.S. Environmental Protection Agency

4. **Laboratory:** National Risk Management Research Laboratory

5. **Project ID:** #252

6. **Problem Statement:**

Ocean tankers and storage tanks for petroleum products such as gasoline, diesel fuel, or aviation fuel, emit a large amount of the lighter fraction of the fuel through evaporation during filling and storage process. While the evaporative losses can be a health-hazard to workers and the neighborhood, the economic loss is large and unnecessary. Thin-film non-porous membranes specially made of a hydrophobic resin are capable of recovering the volatile organic compounds (VOCs) from petroleum for direct recycle/reuse. In the vapor permeation process, the VOCs are removed from the VOC-air mixture and condensed back to a liquid phase with very high selectivity. The objective of this project is to develop a cost-effective, pollution prevention based technology suitable for preventing the loss of fuel hydrocarbon components to the atmosphere during fuel transfer operations, refueling operations, and fuel storage.

This project supports the DoD's Tri-service Environmental Quality R&D Strategic Thrust Area 2A.2 Air Organic and will partially meet, or contribute to several DoD user requirements specifically User Requirement 2I.1g Control/Reduce VOC Emissions from Fuel Storage/Fueling. It may in part also have a role in contributing to User Requirement 3.905 Flow Reduction and VOC Emissions Control for High Volume-Low Concentration Sources.

7. **Project Description:**

VOCs from air can be recovered by simple condensation. When the VOC in the air is dilute, which would be the case when VOCs are lost to air during filling a tanker or a storage tank, direct condensation with existing heat exchange equipment is not practical because of the large air volume involved. It, would however, be economical if the VOCs can be concentrated by a factor of 1000 or more before condensing. Such is the purpose of the use of vapor permeation membranes.

The process of vapor permeation is very similar to pervaporation, which is usually reserved for VOC-recovery from a liquid stream. In both processes, the membrane is hydrophobic and non-porous. In the vapor permeation process, the VOCs are removed from the VOC-air mixture and condensed back to a liquid phase with very high selectivity. The hydrophobic VOC's must first

dissolve in the membrane itself. This phenomenon of adsorption is characterized by Henry's Law, and a constant, Henry's Law constant, that represents the efficiency of adsorption. The VOC then diffuses through the thickness of the membranes and finally desorbs at the permeating side of the membrane. A vacuum is usually applied to the permeate side of the membrane and the VOC's and water are separated from the low pressure exhaust stream by condensation. An inert gas sweep can also be used to achieve similar, and in some cases, superior results. The energy for evaporation generally needs to be provided, although in the case of vapor permeation, the energy demand is much lower than prevaporation, since the VOCs are already in a vapor phase.

Some research has been done on the recovery of VOCs, chiefly chlorofluorcarbons (CFCs), from air by vapor permeation process. This research project involves extending this technology to petroleum hydrocarbons as an approach to controlling evaporative fuel emissions. The major project tasks are: bench-scale laboratory tests to define the separation capability of selected membranes and their performance using various levels of vacuum and inert gas sweep, design of a prototype system suitable for demonstration at an appropriate DoD facility, field demonstration of the prototype, and finally engineering analysis of the results including a performance analysis to determine cost performance and payback period.

8. Expected Payoff:

The VOC removal is needed to reduce the formation of photochemical smog and ozone formation, allowing DoD facilities to meet reduction goals in non-attainment areas and also to achieve economic benefits by reducing fuel losses in hot weather zones. Successful development of this technology will provide a cost-effective approach to eliminate a source of hydrocarbon emissions to the atmosphere, thus reducing photochemical smog formation, ozone formation and evaporative fuel losses during fuel handling and storage. We expect fuel loss avoidance to more than pay for the total costs, including energy penalty costs, of other control techniques, which would be required to control emissions in areas requiring such controls, particularly California.

9. Milestones/Accomplishments:

1. Complete preliminary technical plan for FY95 work and overall 2-year outline — 04/95
2. Visit Naval Facilities Engineering Science Center (NFESC) at Port Hueneme for detailed discussion of technical plan and outline/begin effort to set objectives for prototype based on emission regulations — 04/96
3. Complete details in house experimental plan for membrane screening based on simulated VOC emissions of interest targeted by client. Tests are to determine transport rates, selectivity and separation factors for individual and mixed vapors — 07/95
4. Complete detailed experimental plan — 07/95
5. Procure hollow fiber membrane modules and complete assembly of experimental equipment — 08/95
6. Complete laboratory experiments for screening membrane effectiveness — 01/96
7. Complete laboratory data analysis — 03/96
8. Complete model development to predict performance of the hollow fiber module — 05/96

9. Complete Phase I interim progress report	05/96
10. Begin prototype design based on lab studies	04/96
11. Acquire contractor for demo	09/96
12. Acquire prototype for demo	12/96
13. Complete test site selection	02/97
14. Develop test plan for demo	04/97
15. Conduct test plan for demo	06/97
16. Complete system design model using prototype and lab test data	08/97
17. Complete Final Report	12/97

A bench-scale vapor permeation apparatus has been built for the selective separation of gasoline vapors from a nitrogen gas stream. The separation unit is based on a hollow fiber module having a membrane surface with an ultrathin silicone coating. An analytical method for the simultaneous determination of the amount of the various gasoline vapor components and nitrogen from a single sample injection has been developed. A test plan, including a Quality Assurance plan has been completed. A model gasoline vapor mixture has been developed to represent the gasoline components and their respective concentrations encountered in a storage tank vent. A number of preliminary experiments have been performed to explore the effectiveness of the membrane separation apparatus under various operating conditions and removal configurations. To date excellent removal performance for pentane and hexane have been observed; however the performance for butane is not yet acceptable. Experimental work on some alternative equipment configurations is underway to explore options for increasing efficiency.

10. Transition Plan:

Design data and results of demonstrations will be provided to DoD during the third year. The project will be coordinated with the NFESC for the development of User Data Packages and technology transfer needed to communicate the technology development results in a form that will enhance DoD-WIDW exploitation. Although newly formed, the NFESC has excellent capabilities to assist in the RD&E efforts and will become the primary technology transfer vehicle as the technology moves from the research through the field study phase.

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	TOTAL
SERDP	250	100	400	200	950

12. Performers:

This research project is coordinated by the National Risk Management Research Laboratory/ORD/USEPA. The Naval Facilities Engineering Service Center will collaborate with the NRMRL to (1) identify fuel types of concern; (2) identify candidate demonstration sites; (3) select the demonstration location; (4) coordinate site access and activities and will closely monitor the pilot and demonstration work to ensure the sources needs are adequately met.

The NRMRL is conducting bench-scale research in its laboratory facilities to characterize the chemical composition of VOC emissions from petroleum fuels, to determine the kind of membranes needed to apply vapor permeation, and to develop data for the design of a scaled-up prototype.

The Northeast Hazardous Substance Research Center, New Jersey Institute of Technology has extensive experience in the development of membrane technology and applications to solve environmental problems. The Center is responsible for: (1) conduction bench-scale testing of certain membranes for vapor permeation performance; (2) designing and fabricating a scaled-up prototype system; (3) demonstration of the prototype at a suitable DoD facility, and (4) preparing an economic analysis to determine the capital and operating costs and payback periods for a range of full-scale applications.

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14. Keywords:

Pervaporation, Vapor Permeation, Hydrophobic Membrane, Hydrocarbon Recovery.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Advanced Mass Spectrometry for Atmospheric Monitoring

3. **Agency:** US Air Force

4. **Laboratory:** Armstrong Laboratory, AL/XP

5. **Project ID:** #192

6. **Problem Statement:**

The need for accurate measurements of the identity, concentration, and spatial distribution of atmospheric pollutant species is fundamental to many areas of environmental research and development and crosses the boundaries of several of the SERDP pillars:

- Compliance with standards for emission of pollutants into the air from waste sites, rocket and jet engine operations, power plants, manufacturing and weapons destruction facilities, etc., can only be demonstrated by the use of reliable measurements of the emissions.

- Air pollution reduction efforts must be founded on accurate assessments of current emission levels and must be monitored for effectiveness.

- Cleanup of underground hazardous waste sites requires first that the sites be found and characterized. Detection of airborne emissions from such sites is an efficient and cost-effective alternative to traditional bore hole drilling methods.

The goal of the research proposed here is to develop and demonstrate technology to measure the concentrations of essentially all neutral species in the atmosphere at ground level, in the troposphere, and in the stratosphere. Traditional mass spectrometry for detection of major pollutant species such as CO_2 and NO_x will be combined in a single instrument with a novel chemical ionization technique for ultra-high sensitivity detection of trace neutrals. The technique is broadly applicable to the many requirements listed above, is adaptable to field measurements on the ground and on research aircraft, is low risk, and provides greater than 10^{12} dynamic range with part-per-trillion sensitivity.

7. **Project Description:**

Approach: In recent years the range of techniques available for analysis of natural and pollutant species in the troposphere and stratosphere has expanded. In particular, ion mass spectrometry techniques have become much more sensitive and, in combination with laboratory kinetics measurements, have led to the quantitative analysis of trace neutral species present in

concentrations much too small for direct measurement by traditional mass spectrometry.

Chemical reactions between neutral pollutant gas molecules and the ions that are naturally present in the atmosphere frequently produce new ion species that are unique signatures of the original trace neutral. Detection of the product ion species unambiguously shows the presence of the original neutral. The concentration of the neutral species can be calculated from the intensities of the reactant and product ions measured in the atmospheric environment of interest and from measurements of the rate coefficients of the relevant ion-molecule reactions. This technique has been used to determine the concentrations of such species as sulfuric acid, nitric acid, pyridine, and picoline in the unperturbed atmosphere and to measure the concentration of the important hydroxyl radical (OH), which cannot be detected easily by other methods. Because of the very small background signal level for ions, the technique routinely gives sensitivities in the part-per-trillion range and can sometimes be optimized to detect neutrals in parts-per-quadrillion.

Several novel techniques for making very high sensitivity measurements of ions in the atmosphere have been pioneered by F. Eisele. In the simplest of these, a flow of gas at atmospheric pressure is brought into a high voltage drift tube in which the drift direction for the ions of interest opposes the neutral flow direction. The ions are slowed down, extracted from the primary neutral flow, and directed toward a sampling orifice. The ions then enter a high vacuum region of the apparatus and are detected with a pulse counting quadruple mass spectrometer. The concentrations of the neutrals of interest are calculated from the signals of their product ions generated in reactions with ambient charged species. In a variation of the method, ambient ions are excluded from the flow tube, and specific test ions are injected into the neutral flow to create unique product ions that are detected the same way. Eisele (Georgia Tech and NCAR) is currently under contract to us using FY92 SERDP funds to make initial measurements of ion composition in rocket and jet plumes and will make the first measurements in the spring of 1994. In a collaborative effort closely related to this SERDP proposal, one of the members of our in-house research team is currently investigating the ion chemistry of jet engine plumes at the Max Planck Institute for Atomic Physics in Heidelberg, Germany, under the AFOSR Window-on-Europe program.

Our in-house mass spectrometer development effort will focus on incorporating Eisele's novel chemical ionization techniques into a quadruple mass spectrometer used for standard measurements of neutral composition at atmospheric pressure. In addition to the ultra-high sensitivity techniques described above, the instrument will also provide variable energy electron impact ionization with differential pumping for detection of the major pollutant species. The portable instrument package will be easily adaptable to field and flight experiments. We have used basic research funding to construct the high vacuum portion of the instrument, containing the mass spectrometer, detectors, differential pumping stages, and electronics and data handling equipment. The sampling flow-drift tube system is currently being designed. SERDP funding will be used primarily to complete the design and assembly of the sampling system, to integrate and test the sampling system, and to make the initial field measurements.

Laboratory measurements of ion chemical rate constants will be made in an existing variable temperature selected ion flow-drift tube (SIFDT), which is the only such instrument available in

any DoD laboratory, and in a new high temperature flowing afterglow apparatus, which is the only such instrument anywhere in the world. These types of apparatus have provided most of the previous measurements of the chemical kinetics important in atmospheric ion chemistry. The specific species and reactions to be studied will be chosen after measurements of ion composition in the field are started. We expect that the ion chemistry of trace pollutant species will pose new challenges to the laboratory measurement program. Although the bulk of funding for the laboratory effort is provided by the Air Force Office of Scientific Research, some SERDP funding may be used in future years to develop new laboratory techniques required to make measurements of specific pollutant species under the extremes of temperature and pressure represented in the actual atmospheric environments.

SERDP funding in FY93 has been used in the laboratory program to develop an ion chemical technique for detection of chlorine nitrate, $ClONO_2$, and to determine the atmospheric lifetimes of perfluorocarbons, which have been proposed as substitutes for ozone depleting chlorofluorocarbons. In a related SBIR Phase II research effort, the heterogeneous decomposition of halocarbons on Al_2O_3 particles from solid fuel rocket engines is being investigated.

The effort proposed here directly supports many of the requirements listed in the Tri-Service Environmental Quality R & D Strategic Plan, including:

Pillar 1, Clean-up:	Thrust 1.C: "Characterization/ Monitoring,"
	Thrust 1.D: "Chemical Analytical Systems;"
Pillar X:	Thrust X.1: "Hazard Assessment;"
Pillar 2, Compliance:	Thrust 2.A.2: "Routine Emissions,"
	Thrust 2.A.3: "Detection and Monitoring,"
	Thrust 2.C: "Manufacturing and Disposal,"
	Thrust 2.0: "Compliance Evaluation;"
Pillar 3: Pollution Prevention:	Thrust 3.N: "Reduce Greenhouse Gas Emissions."

Our research group has been studying atmospheric ion composition and charged particle chemistry as its core research effort for several years. Applying this experience to specific environmental problems using SERDP funding will therefore be highly leveraged with other funding sources. Specific tasks that will be accomplished with the SERDP funds are:

1) Use existing high sensitivity atmospheric ion detection equipment (Eisele, Georgia Tech, NCAR) to measure ion composition in jet engine exhaust plumes.
2) Develop in-house mass spectrometric capability based on Eisele's techniques; test and calibrate instrumentation in concert with complementary techniques; demonstrate usefulness of technology in field tests using jet engine exhausts, rocket exhausts, and other measurements of opportunity.
3) Perform laboratory measurements of the kinetics of the ion chemistry of trace neutral pollutant species as required to calculate the concentrations of the pollutants measured in the field programs.

8. Expected Payoff:

The Geophysics Directorate of the Phillips Laboratory is an acknowledged world leader in measuring the chemical kinetic properties of ion-molecule, ion-ion, electron-molecule and electron-ion reactions relevant to atmospheric, ionospheric and high temperature plasma processes, and in measuring the ion composition of these environments with mass spectrometers. For this work, our research group was selected to be one of the 1991-1993, and 1994 to present, Air Force Office of Scientific Research (AFOSR) Star Teams recognizing excellence in basic research relevant to Air Force requirements. The Geophysics Directorate is the only DoD laboratory facility where the in-house expertise in ion chemistry and mass spectrometry can be brought together to develop the high sensitivity trace neutral detection method that we propose.

We plan to focus our efforts initially on the effluents from jet and rocket engine operations in the troposphere and stratosphere. In order to assess the environmental impact of the pollutant species generated by the combustion process in such engines, the concentrations and lifetimes of the foreign species and the chemistry which they undergo in the atmosphere must be understood. Our proposed research program will lead to high sensitivity measurements of the concentrations of many species in the atmosphere. Models of the chemistry of polluted environments can then be improved by adjusting the model to match the measurements. The validated models can then be applied with confidence to environmental scenarios where direct measurements have not been made and will also lead the way to future research needs. The immediate benefit of the research will be to ensure compliance of jet or rocket engine emissions with mandated standards, to point the way to problems that might cause high emissions, and in general to support DoD efforts to reduce pollution from jet and rocket operations.

In addition, we expect that our ion chemistry technique will be broadly applicable to other requirements for environmental monitoring in the areas of compliance, cleanup, and pollution prevention. We will actively seek opportunities to bring the techniques developed in this research effort to collaborative field campaigns where other complementary trace gas detection techniques are deployed. Comparison and cross-calibration of many techniques will ultimately lead to a battery of instruments which between them can detect pollutant species under more varied environmental conditions than any one technique could alone.

9. Milestones/Accomplishments:

1.	Complete first measurements of jet plume composition; F15 jet at Eglin AFB	07/94
2.	Determine direct neutral performance and sensitivity	12/94
3.	Determine ion performance and sensitivity	06/95
4.	Perform first field-scale demonstration; measurements board a T-39 jet at Wallop Flight Facility	06/95
5.	Complete design of high pressure laboratory flow tube	01/96
6.	Integrate lightweight high performance instrument into aircraft platform for jet engine exhaust sampling	04/96
7.	Perform jet exhaust measurements	06/96
8.	Complete attachment rate measurements for chemical ion reagents	08/96

9. Perform second field-scale demonstration 12/96
10. Complete commercialization prototype 09/97
11. Perform validation comparison measurements 04/98

To date, tremendous progress has been achieved in translating a highly capable, but fragile and expensive laboratory technique into a robust and portable instrument. Initial measurements of jet exhaust emissions have been obtained on the ground behind operational F15 aircraft. An initial campaign was conducted aboard a T-39 aircraft platform to measure exhaust products behind a T-38 from a 0.4 km to 5 km at altitudes ranging form 15,000 feet to 40,000 feet. The instrument has already been able to measure such gas species as HCN at the 0.4 part-per-billion level. To date, this instrument technique is nearly the only one available for measuring acid emissions from aircraft under realistic conditions. We have already found applications for the instrumentation in NASA and Air Force research programs. Four scientific papers have appeared in print in Science, Journal of Geophysical Research, and Journal of Chemical Physics.

10. Transition Plan:

The end product of this proposed research will be a portable, highly sensitive, calibrated and tested instrument for determining trace neutral composition in polluted regions of the atmosphere. This product should be suitable for commercialization and sale to the environmental monitoring community, and we will actively seek industry partners interested in developing this technology with us via CRADA agreements or other appropriate vehicles.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	320	665	150	400	600	600	2,415
AFOSR	400	400	400	400	400		2,000
TOTAL	720	1,065	550	800	1,000	600	4,415

12. Performers:

Development of the portable mass spectrometer equipment, measurement of relevant ion chemical kinetics, and analysis of all data will be performed at the Ionospheric Interactions Branch, Geophysics Directorate, Phillips Laboratory, Hanscom AFB, Massachusetts. Georgia Tech and the National Center for Atmospheric Research (NCAR) has been under contract to us to make initial measurements of ion composition in jet engine exhaust plumes. The Max Planck Institüt für Kernphysik, Heidelberg, Germany, will be an unfunded collaborator.

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14. Keywords:

Ion Chemistry, Mass Spectrometry, Airborne Pollutants, Detection, Atmosphere/Troposphere/Stratosphere, High Sensitivity.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Leak Location in Underground Pipelines
3. **Agency:** U.S. Environmental Protection Agency
4. **Laboratory:** National Risk Management Research Laboratory (NRMRL)
5. **Project ID:** #249
6. **Problem Statement:**

The goal of this applied research and technology development effort is to develop and demonstrate a portable and on-line acoustic leak detection/leak location system to accurately and reliably test single and double walled pipelines of various sizes and content (i.e., gasoline, diesel, jet fuel, potable water, low level liquid wastes, etc.) Such a system would not only assist the regulated community in complying with existing state and Federal regulations but would also reduce the spread of contamination and loss of drinking water through early and more accurate leak detection/location.

Existing Federal regulations (40 CFR Parts 280 and 281, September 1988) require that underground tanks and pressurized pipelines containing petroleum and other hazardous substances be tested for leaks on a regular basis and that once a leak is detected it must be mitigated. This is an onerous task when one considers the enormous number of miles of pipeline associated with retail gasoline service stations nationwide, airport hydrant systems, Army and Navy fueling depots, DOE low level liquid waste systems, etc. Over 300,000 releases from underground storage systems have been confirmed to date and the EPA estimates that as many as 15 to 20% of the approximately 1.8 million regulated underground systems nationwide either are leaking or are expected to leak in the near future. The environmental threat from these leaking systems has a direct impact on public health because approximately half of the Nation's drinking water supply comes from ground water. Small quantities of gasoline released underground can contaminate millions of gallons of potable ground water with suspected carcinogens such as benzene, etc. The threat is not limited to ground water; leaking petroleum and chemicals can also contaminate surface waters and contribute to air pollution. In addition, these products release vapors that can seep into the sewerage systems of homes and businesses and accumulate to explosive levels. Besides the environmental threats and astronomical costs associated with addressing these threats (over $30.0 billion for site remediation alone) we are also wasting valuable drinking water and energy resources.

Rapid and cost-efficient remediation can occur if the source of an underground leak can be pinpointed quickly and accurately. Current technologies utilizing volumetric- and pressure-based methods are unable to effectively accomplish this objective. Since 1990, EPA's NRMRL has been conducting applied research on acoustic technology for rapid, near-real-time leak

detection/location in pressurized pipelines typical of those found at retail service stations. Results of this work indicate that acoustic measurements combined with advanced signal processing methods can provide a means by which to detect and locate small leaks over long distances in pressurized pipelines. Additional applied research and technology development work is required to optimize system performance and application on larger and longer lines and on lines of different configuration. A Science Advisory Board Review (June 1992) of this earlier work (which was funded solely with EPA/ORD funds) recommended continued research in this area.

7. Project Description:

In 1990, EPA's National Risk Management Research Laboratory initiated a program to develop a non-invasive, non-destructive method for detecting and locating small leaks in pressurized pipelines containing petroleum products. Experiments were conducted at the UST/Pipeline Test Facility in Edison, New Jersey in which three acoustic sensors separated by a maximum distance of 125 ft were used to monitor signals produced by 3.0, 1.5, and 1.0 gal/hr leaks in the wall of a 2 inch diameter petroleum pipeline. Line pressures ranged from 10 to 30 psi. Application of a leak location algorithm based upon the technique of coherence function analysis resulted in mean differences between predicted and actual leak locations of approximately 4 inches. This is a significant improvement over current techniques and provides results in a matter of minutes; however, additional experiments with higher pressures and over longer and larger pipelines are required to optimize system performance and expand system application.

The objective of this proposal is to develop, design, fabricate, and demonstrate both a portable and an on-line passive acoustic leak detection/location system that can be used on: (1) existing pipelines, (2) pipeline systems that cannot be breached, (3) newly installed systems, and (4) double-walled pipelines. To meet this objective, a three-phased development and demonstration program will be conducted over a three year period.

Phase I: Modifications to UST/Pipeline Test Facility and Preliminary Experiments: This phase will involve (a) modification of the existing UST pipeline system to make it more representative of systems found at retail service stations, (b) design and installation of a double-walled steel pipeline system typical of DOE systems used to transport low level liquid wastes, and (c) design and installation of a large diameter (10-12 inches) and longer (300-500 ft.) high pressure pipeline system typical of Army and Navy facilities.

Detailed experiments will be conducted on the representative pipeline systems to determine the accuracy and performance of acoustic technology for locating leaks of differing sizes over variable distances and to identify and evaluate potential differences in performance due to pipeline configuration. Experiments will be designed and conducted to optimize and validate the previously developed "breadboard" system which is based on a coherence function analysis approach; and to evaluate other approaches such as signal attenuation, time of flight, and cross-correlation analysis. The performance of the location system as a function of leak flow rate, line pressure, pipeline diameter, and pipeline length will be determined and validated. Based upon these experiments, recommendations will be made to modify/redesign the existing "breadboard" system.

A protocol appropriate for each pipeline configuration will also be developed for field application of the modified system. The protocol(s) will be based on the current test method which will be refined through selective studies to address questions such as: (a) when testing on longer and wider pipelines, are additional sensors necessary to characterize the signal created by the leak and at what intervals must the sensors be spaced; (b) how will the signal be affected by leaking valves, changes in pipeline connection hardware, multiple bends and elbows, corrosion anomalies, etc.; and (c) what are the affects of multiple leaks?

Phase II: Prototype Development and Demonstration: Based upon the recommendations of Phase I, a portable acoustic leak detection/location prototype system will be designed and fabricated. The system will enable field testing of pipelines with minimal interruption to commercial operations; most tests will take less than one hour to perform. Using the protocol(s) developed in Phase I, additional "shakedown" testing of the prototype system will be conducted at the UST/Pipeline Test Facility and field validation will be accomplished at actual retail service stations, and Army, Navy, and DOE sites of opportunity.

Phase II will also include initiation of the development of an on-line automatic acoustic system that can be attached to existing pipeline systems or integrated into new systems (single or double-walled) during installation. This would provide constant monitoring with an immediate release detection/location information alarm. System hardware will be developed and preliminary experiments will be conducted on the respective test pipeline systems to identify and evaluate performance characteristics associated with an on-line monitoring system. Recommendations will be provided for prototype design and fabrication, and a protocol will be developed for field application.

Phase III: Final Prototypes and Users Manual: During this phase, final modifications and refinements will be made to the portable acoustic leak detection/location system hardware and software. The system may be further field tested if significant modifications are made and further optimization is required. This effort will result in a user friendly, field applications manual and a final prototype and hardware system (including software) ready for commercial application.

Phase III will also involve fabrication of the on-line prototype leak location/detection system. The system will be evaluated for performance and accuracy on the respective test pipeline configurations. Studies will include signal characterization and algorithm verification. Based on these results, the on-line system software program will be modified and refined. Final field validation of the on-line system will be conducted at new installations or recently upgraded installations (as per the regulations) at DOE, Army, and Navy facilities. The final prototype will then be developed for commercial application.

8. Expected Payoff:

Underground pipelines are used by numerous industries worldwide to transfer liquid products. Presently, only two methods are used to locate leaks in pipelines. The first involves uncovering the line and performing a visual inspection. This is very disruptive to operations, destructive to

facility hardware, time consuming and costly. The second method uses a helium or halogen tracer. This technique has serious operational and performance problems, and is also time consuming and costly. Passive acoustic leak detection/location provides an accurate and cost effective workable solution to this problem. Pipelines can be tested in minutes rather than days. Leaks can be located in any line without having to use invasive techniques which are especially costly in low-level radioactive wastelines typically found at DOE facilities. Furthermore, the cost of remediations will diminish significantly as releases are detected earlier and the amount of excavation associated with a repair is reduced. Most importantly, with more accurate on-line monitoring capabilities, there is better control over product transfer systems, resulting in the prevention of millions of gallons of fuel being released to the environment (and subsequently resulting in the reduction of irreparable damage to our natural resources) and the conservation of a limited energy resource.

9. Milestones/Accomplishments:

1.	Program Start	01/95
2.	Advisory Committees Established	01/95
3.	Determine Regulatory and Performance Criteria and Operating Conditions	03/95
4.	Conduct Literature Search and Report on State of the Art	04/95
5.	Develop Design Criteria and Initiate Modifications to Test Apparatus	04/95
6.	Interim Report on Bench-scale Evaluations and Field Tests of commercial Technologies	01/96
7.	Complete Part of Modifications to Test Apparatus	07/96
8.	Interim Report on Correlation of Bench-scale and Test Apparatus Results	10/96
9.	Initiate Field Evaluation of Prototype Portable System	09/96
10.	Conduct Rest of Modifications to Test Apparatus	09/96
11.	Modify Portable System and Evaluate Under Controlled Conditions at Test Apparatus	12/96
12.	Demonstrate Modified Portable System at Appropriate DoD and DOE Facilities	02/97

The design firm, Fluor Daniel, has developed an initial plan for modification of the experimental test pipeline apparatus at the EPA storage system test site in Edison, NJ. The state-of-the-art report has been issued although is expected to be updated as the project continues. Initial leak signal measurements have been initiated at Iowa State Univ and a program of bench scale studies critical to the efficient conduct of the project is being refined.

10. Transition Plan:

Once the technology has been developed, the National Leak Prevention Association, National Leak Detection Association, American Petroleum Institute, National Association of Corrosion Engineers, and the participating agencies in this project will actively market this technology to their constituents. In addition, the EPA will pursue commercialization through the Federal Technology Transfer Act mechanism. There is a great deal of interest in using this technology by the commercial sector due to the tremendous cost savings that may be realized from immediate location of releases, more timely remediations, and conservation of fuel (energy). In

addition, the technology has cross-application to pipeline systems involving other contents such as gas, water, sewage, etc.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	Total
SERDP	1,921	800	79	800	3,600
EPA	250	250	250	0	950
DOE	200	200	200	0	600
NAVY	150	0	0	0	150
TOTAL	2,521	1,250	529	800	5,300

12. Performers:

This project will be conducted by EPA's National Risk Management Research Laboratory in conjunction with DOE's Oak Ridge National Laboratory, the Naval Facilities Engineering Service Center, Port Hueneme, CA, and the Army Civil Engineering Research Laboratory, Champaign, IL. The project will be coordinated through an Interagency Agreement, whose performers and sponsors will include: U.S. Environmental Protection Agency: David Ziegle, Director, Office of Underground Storage Tanks, Washington, DC; Anthony N. Tafuri, James J. Yezzi, Underground Storage, Tank Program, National Risk Management Research Laboratory, Edison, NJ; U.S. Navy: Elsie L. Munsell, Deputy Assistant Secretary of the Navy, Washington, DC; Ted Zagrobelney, Division Director, Naval Facilities Engineering, Command, Washington, DC; Leslie Karr, Environmental Engineer, Naval Facilities Engineering Service Center, Port Hueneme, CA; U.S. Army: Vincent Hock, Metallurgist, U.S. Army Civil Engineering, Research Laboratory, Champaign, IL; Major Mike McDevitt, Program Manager, U.S. Army Civil Engineering Research Laboratory, Champaign, IL; U.S. Department of Energy: Sherry Gibson, Program Director, Department of Energy, Washington, DC; Jackie Noble-Dial, Program Manager, Oak Ridge National Laboratory, Oak Ridge, TN.

13. Principal Investigators:

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14. Keywords:

Acoustics; Leak Detection; Underground Storage Tanks; Pipelines; Petroleum; Remediation

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Reduction of Environmental Noise from Jet Engine Hush Houses

3. **Agency:** U.S. Air Force

4. **Laboratory:** Occupational and Environmental Health Directorate, Armstrong Lab (AL)

5. **Project ID:** #1051

6. **Problem Statement:**

Afterburning jet engines are a powerful source of noise. Hush houses and jet engine test cells are commonly used on air bases and at test facilities for testing and maintenance applications where jet engines are run at, or near, full power. A hush house typically consists of a hanger which contains the aircraft or out-of-airframe jet engine. The hanger is provided with an acoustically lined augmenter tube behind the hanger to contain and silence the jet engine exhaust (passive silencer). At the outlet of the augmenter tube there is a 45° ramped deflection plate to deflect the exhaust stream from a horizontal to a vertical direction. While traditional passive exhaust silencers utilized in these facilities provide good high frequency sound attenuation, they provide practically no sound attenuation at low frequencies (8 to 80 Hz). Consequently, the unattenuated low frequency noise emanating from such a test facility is a serious problem. Air Force representatives have stated that a minimum of 12 air bases have significant problems with low frequency noise from hush houses or jet engine test cells. The low frequency noise levels measured at 250 feet from an Air Force hush house may be 106 dB, which is 26 dB above the threshold of rattling for lightweight buildings. To avoid rattling in this case, lightweight buildings would need to be placed no less than 5000 feet, nearly 1 mile, from the hush house.

The most promising concept for significantly improving the low frequency noise attenuation of hush houses and jet engine test cells is to replace one or more of the acoustically lined sections of the augmenter tube with sections containing active noise control systems. The active section incorporates microphones and speakers which serve respectively as sensors and actuators in the control system. These are mounted circumferentially behind a porous resistive liner and out of the exhaust flow. Active noise control works very well at the low frequencies of concern here. Locating the microphones and speakers out of the exhaust flow significantly reduces their exposure to the exhaust stream and causes no increase in back-pressure, as with some passive systems. This approach provides superior performance at low frequencies with no significant reduction in high frequency attenuations, while maintaining the same physical envelope of the all-passive system.

The proof-of-principal of this concept was successfully demonstrated in 1994 under a project conducted by the Air Force using funds provided by SERDP. The scope of that project was to design, develop and evaluate a quarter-scale model of an active silencer for use in hush house

or jet engine test cell augmenter tubes. The goal was to prove the principle of using an active liner section in a hush house augmenter silencer tube to substantially reduce the low frequency noise generated by jet engines being tested in the hush house.

In this project, a quarter-scale augmenter tube consisting of three passive sections and an active section was designed and fabricated. The model was mounted in a low speed wind tunnel and tested under a variety of test conditions, including:

- Independent and coupled speaker control;
- Feedforward and feedback control;
- Use of two different types of controllers-single input single output (SISO) and multiple input multiple output (MIMO); and
- Flow versus no-flow conditions in the wind tunnel.

The results demonstrated experimentally the feasibility of obtaining up to 12 dB of reduction in low frequency noise by inserting a single active liner section into a typical hush house augmenter tube silencer. Greater noise attenuation can be achieved by inserting additional active sections.

7. Project Description:

While these results proved the basic principle of actively controlling low frequency noise in an augmenter tube, there are a number of other developmental issues that must be addressed before this concept is fully proven and ready for prototyping and full scale engineering development in hush houses and jet engine test cells.

The tests described above were all conducted at ambient temperatures. An operational system must work when exposed to the hot; corrosive exhaust gases moving at high velocity that are present in the augmenter tube, estimated at about 750° F in the region of interest. Microphones must be carefully selected and speakers must be developed to operate in this environment. The acoustic and aerothermal effects of the hot flow system must be understood and accommodated in the design of the active liner. Particular aerothermal questions that need to be addressed include:

- Determining the thermal exposure of the microphones and speakers for the active silencer to steady state and transient exposure (thermal shock);

- Determining the exposure of microphones and speakers to static pressure during various engine run conditions and to the transient pressure pulse at the onset of afterburner runs; and

- Determining the content of exhaust gases in terms of corrosive effects on materials.

There are two sources of low frequency noise within the hush house. The first is the noise generated by the mixing and turbulence of the hot exhaust gases with the ambient temperature gas within the augmenter tube. The second is the noise generated by the exhaust flow passing over the lip of the 45° exhaust ramp located at the end of the augmenter tube. The former noise will be controlled by the proposed active liner. The later noise will be controlled by attaching a sawtooth flange to the lip of the exhaust ramp; this will break up the large scale turbulence which generated the low frequency noise. The higher frequency noise is more readily dissipated in the atmosphere. Acoustic questions that must then be addressed include:

- Quantifying the maximum exposure of microphones and speakers to jet engine exhaust noise;

- Determining the extent that microphone array and signal processing equipment are capable of differentiating between low frequency jet noise and convected turbulent pressure fluctuations;

- Characterizing noise generation and propagation in order to determine the optimal axial location for the active liner segments;

- Quantifying the volume displacement requirements for the high temperature speakers of the active liner; and

- Determining the extent of low frequency noise generation by the exit flow at the trailing edge of the 45° exit ramp.

There also are a number of mechanical and electrical design developments that must be addressed, including:

- Developing a speaker/actuator that will provide the required volume velocity at low frequency and operate reliably in the high temperature augmenter tube environment;

- Selection of the proper control algorithms for the active controller;

- Optimizing the liner resistance; and

- Determining the optimum placement and number of microphones and speakers.

The technical approach will take several parallel paths to address the development issues discussed above. This approach will culminate in the installation of a single active noise control section into an operational hush house augmenter tube for a full-scale proof-of-concept demonstration.

Additional tests will be performed on the quarter-scale model mounted in the low speed wind tunnel. The original tests described above proved the principle of operation. However, there

were no attempts to optimize either the control parameters or the resistance of the liner. These additional wind tunnel tests will be used to optimize these parameters. Scale model tests also will be performed in the wind tunnel to evaluate various types of sawtooth trailing edge configurations for the 45° exit ramp.

Existing data taken on an augmenter tube will be reviewed and a series of measurements will be performed on a full-scale, operational hush house, such as that used by the 944th Fighter Wing at Luke AFB. These tests will include full-scale measurements to quantify the exhaust environment within the augmenter tube (e.g., temperature and temperature gradient, flow rate, pressure, transient pressure pulse at onset of afterburner, gas composition.).

A sawtooth trailing edge will be installed onto the exit ramp of the hush house to minimize the flow-generated noise and to measure its effectiveness. With the sawtooth trailing edge installed, the low frequency acoustic spectrum about the hush house will be measured to (1) isolate the edge effects from the engine exhaust effects, and (2) provide baseline data for later comparison with the demonstration system.

High temperature loudspeakers currently under development, will be modified to (1) work at lower frequencies, and (2) provide a greater volume velocity so that it can be used in the proposed hush house application. Several of these speakers will be fabricated for use in the proposed effort.

Commercially available high temperature microphones will be evaluated and appropriate microphones for this application will be selected.

Selected speakers and microphones will be installed in an operational hush house to test their durability in this hot, corrosive environment. The effects of both steady state and transient aerothermal exposures will be investigated.

Finally, a full-scale active liner section for an operational hush house augmenter tube will be fabricated and installed, and its effectiveness in an operational environment will be measured. There have been preliminary discussions with Colonel William Ponder, Commander of the 944th Fighter Wing at Luke AFB, concerning the use of their hush house for these tests, and he has offered to make the hush house under his command available for this proof-of-concept installation and test program.

This project is in support of the Compliance Pillar in the Tri-Service Environmental R&D Strategic Plan.

8. Expected Payoff:

Use of an active silencer on hush houses offers significant benefits to the military in land utilization at air bases. A reduction of 7.5 dB of low frequency noise from a hush house would regain 1400 acres and a reduction of 15 dB would regain 1700 acres of the land surrounding the facility for unrestricted use. This offers a significant gain in the use of expensive air base real

estate.

Another significant benefit is the ability to operate hush houses at night. Currently, operation of many hush houses is restricted to daylight hours. For example, the hush house used for F-16s by the 944th Fighter Wing at Luke AFB is only operated from 07:00 to 18:00 because of concerns of the noise impact on the surrounding community during nighttime operations. The ability to operate 24 hours per day would make the engine repair/maintenance and testing cycle more efficient thereby saving from 30% to 50% in the time and expense normally required.

Finally, the active liner concept has the potential for replacing conventional silencers used in a number of other military and civilian applications, thereby providing improved low frequency attenuation with significant size and wight savings. For example, active silencers using this technology could be used on Navy ships to quiet the exhaust from diesel and gas turbine engines used for propulsion and ship service power generation. Studies performed by the Navy indicate substantial weight savings (over 100,000 pounds per ship for LPD-17 class ships) is possible if active liner silencers were available as replacements for the conventional passive units now used, with the added benefit of improved ship stability when operating in heavy seas (due to weight reduction high in the ship). There are many other potential applications of this technology.

9. Milestones/Accomplishments:

1. Perform Proof-of-Principle 1/4 Scale Model Design and Test	06/94
2. Begin Full Scale Proof-of-Concept Program	08/96
3. Perform Scale Model Wind Tunnel Tests to Optimize Controller, Liner Resistance, and Ramp Trailing Edge Design	11/96
4. Design and Fabricate Full Scale Saw Tooth Ramp Extension	02/97
5. Perform Full Scale Hush House Augmenter Tube Measurements	04/97
6. Design and Fabricate High Temperature Loudspeakers	07/97
7. Select and Procure High Temperature Microphones	07/97
8. Conduct Loudspeaker and Microphone Durability Tests in a Hush House	09/97
9. Design and Fabricate One Full Scale Active Liner Section	03/98
10. Conduct Full scale Proof-of-Concept Tests	06/98
11. Report, Assessment and Management Review	09/98

The proof-of-principle of the active hush house liner was demonstrated in June 1994. A quarter-scale augmenter tube containing one active noise control section was designed and fabricated. This model was mounted in a wind tunnel and tested under a variety of conditions. The results demonstrated experimentally the feasibility of obtaining up to 12 dB of reduction in low frequency noise by inserting a single active liner section into a typical hush house augmenter tube. Additional attenuation will be achieved by using additional active sections.

10. Transition Plan:

The project will go forward to prototype development and test, and ultimately to retrofit system specification and procurement of retrofit hardware for hush house active silencers.

11. Funding: $(K)

	FY 96	FY 97	FY 98	TOTAL
SERDP	450	700	335	1,485

12. Performers:

Participants in the program include Armstrong Laboratory, Luke AFB, and a contractor. Program management will be performed by Armstrong Laboratory. A hush house for full-scale diagnostic testing and for full-scale active liner demonstration tests will be provided by Luke AFB. The contractor will design and fabricate the active hush house liner, and will perform all necessary tests including the final demonstration test.

13. Principal Investigators:

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14. Keywords:

Hush House, Jet Engine Testing, Noise Reduction

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness

3. **Agency:** U.S. Army

4. **Laboratory:** Construction Engineering Research Laboratories (CERL)

5. **Project ID:** #523

6. **Problem Statement:**

Preservation of the Department of Defense (DoD) training, testing and readiness mission requires that DoD be capable of controlling, assessing, managing and monitoring noise problems in the vicinity of its bases and installations. They cannot now consistently do this. The DoD faces continual challenges to planned operations and changes to operations because of negative community responses to the noise created by weapons, helicopters, and aircraft. The direct impact is an insidious loss of training and readiness capability through the closure of ranges and firing points, altered flying, and nighttime curfews. Because of noise, the DoD has lost significant mission capability at over 50 installations. Equally important are delays due to procedural or litigation challenges (as provided for in the National Environmental Policy Act) to environmental impact analysis documents, such as Environmental Assessments (EAs) and Environmental Impact Statements (EISs) that propose changes in DoD operations. Such changes include, for example, introduction of a larger battle tank main gun, introduction of supersonic flying in an area not previously exposed to these operations, changing from an older aircraft or helicopter to a newer one, and increases in nighttime military training. Such challenges are difficult to refute when substantiating information is not available. It is expected that the impacts of environmental noise from military operations will continue to be a significant problem, and with enhanced emphasis on nighttime training, will worsen for the foreseeable future.

DoD needs the ability to predict physical sound levels in the community surrounding an installation due to training activity on post. With such a prediction, training could be conducted at times that are less favorable for sound propagation and thus reduce the community noise exposure. Basic Research is needed to advance our understanding of wave propagation in a turbulent atmospheric (meteorological) medium to augment existing sound prediction tools which currently fail when applied under these conditions.

No present physical models are adequate for predictions in the presence of wind driven turbulence or thermal plumes from solar heating. In these situations, a wave that propagates through atmospheric eddies or thermal drafts experiences refraction and diffraction from its normal path. Predicted focus locations on the ground are moved or diminished and acoustic shadows are insonified via scattering. No theoretical or computational method exists that can

simultaneously account for acoustic wave propagation through anisotropic, inhomogeneous, turbulent media (the outdoor air) in proximity with an irregular surface of complex acoustic impedance (the ground). In terms of human response, the DoD continues to have difficulty meeting NEPA compliance requirements and executing the Air-Installation Compatible Use Zone (AICUZ) and Installation Compatible Use Zone (ICUZ) Programs because there is a lack of adequate scientific data on the effects of environmental noise from DoD operations on the health and welfare of people. The National Environmental Policy Act (NEPA) of 1970 requires federal agencies to predict the expected environmental impacts of their activities.

The DoD requires the ability to assess the combined/cumulative human impacts of joint and/or co-located installations and operations. For example, the DoD has been receiving major challenges to environment impact analysis documents because we do not currently address the combined and cumulative effects of Army and Air Force operations there. Most current community (annoyance) impact assessment methodologies for predicting the effects of aircraft noise on humans rely on annualized average exposure descriptions. These annualized procedures are the day-night A-weighted sound level for fixed-wing aircraft, motor vehicles and most continuous industrial noises, etc. A separate annualized procedure, C-weighted day night average level is applied to blast noise and sonic booms. No method exists to combine these two procedures into one overall assessment. Further, there are serious questions about the efficacy of the current C-weighted procedure for blast and sonic-boom noise. Current methodology combines two categories of noise, blast noise, and sonic boom, together, equally into one assessment. However, the technical basis for this methodology exhibits distinct differences between these categories of sound. Sound character and background ambient present two additional challenges to present assessment methodology.

7. Project Description:

The major purpose of this proposed research and development program is to address the issues described above in a coordinated program involving several major federal agencies including the U.S. Army (USA) and the U.S. Fir Force (USAF), the Department of Transportation (DOT), the Federal Aviation Administration (FAA) and the NASA Langley Research Center. This effort supplements and complements current and planned USA and USAF programs, which only together will provide the funding required to adequately address a series of challenging technical issues. The major focus of this effort is a assessing and mitigating military noise. The combined human effects model is a dose response empirical model that provide the means for DoD to assess and mitigate noise. The propagation research will lead to better analytical physical sound propagation models which will be used to improve the underlying physical predictions of sound for the human effects model. The improved physical prediction model also will be used for direct prediction and warning of high level for noise mitigation purposes. The proposed program is part of the DoD Environmental Quality R&D Plan and is highly rated by the user community. It relates directly to Project Reliance DoD Pillar 2: Compliance (Reliance Sub-area: Noise) and covers several requirements. It addresses several of the Research and Development Objectives of the Compliance Pillar, as listed in the SERDP Strategic Guidance which was provided to prospective proposers to the SERDP program. This program will build on previous research by USA, USAF, FAA, and NASA.

Central to control and management of noise are a set of demonstrated methods to reduce noise. This SERDP program continues the 1993 effort to develop a system to forecast high noise levels and thereby provide for inexpensive noise control at training ranges. Central to assessment and monitoring are the technical capabilities to predict the physical noise environment and the expected effects of these environments on human populations. In this project, we will attempt to answer basic questions about acoustic wave propagation through turbulent media:

1) Under what circumstances is multiple scattering theory necessary for accurate predictions?
2) How can the statistical moments of the propagated signal be themselves propagated over a ground surface?
3) What is the effect of propagation through a medium where the turbulence distributions are layered?
4) What is the correlation between atmospheric fluctuations and changes in acoustic propagation?

Results from these approaches will be used to seek a valid approximate model for the influence of turbulence on the average propagation, and for statistics of the fluctuating signal, which will incorporate measured values of wind and temperature versus height.

The combined noise model will be developed in three phases. During Phase 1, an initial combined effects model will be developed based on the current sate-of-the-art. This initial model development will be accomplished through working group consensus building using a contract with NAS and ANSI. By 1997, the initial combined noise effects model, developed by consensus by appropriate cognizant bodies, will be completed. During phase 2, the results of other, related RDT&E by the Army, Air Force and NASA and international partners will be used to revise the Phase 1 preliminary combined noise effects model. During Phase 2, new laboratory and field research will focus on specific issues developed by the NAS and ANSI deliberations and the results from other RDT&E. During Phase 3, the combined noise effects model resulting from Phase 2 will be validated in a series of field tests. Traditional community attitudinal survey techniques will be used at a set of sites where combined noise is received. These might include sites near Army installations which include Air Force air-to-ground gunnery ranges such as Ft. Sill or Ft. Drum. Data collection near Navy or Air Force bombing ranges also will be considered. NAS and ANSI will then be asked to review and approve the final, validated combined noise effects mode.

Research on a high-energy impulsive sound effects model (annoyance) will center on two factors (sub-thrusts) which must be better understood in order to reach the overall gaol of a combined noise effects model. For the first sub-thrust, there will be studies to compare and contrast community response to blast noise and sonic boom. Current methodology combines these two categories of noise into one assessment. Laboratory-field studies of these two sounds in the same test will quantify these differences, if any. For the second sub-thrust, there will be studies to better quantify the role of vibration and rattle in response to these sounds. The technical data strongly indicate that vibration and rattle play a major role in large-energy impulsive noise

annoyance. However, it is not currently possible to quantify an predict the annoyance generated by these factors in combination with the audible sound.

8. Expected Payoff:

Ultimately, results of this program will be used to decrease loss of military mission operational capability through defending against encroachment and decreasing costs associated with compliance with NEPA requirements. The latter will be accompanied by reducing costs associated with defending planned changes in DoD operations. The payoff will be improved training efficiency and operational force readiness.

The benefit/cost associated with encroachment and compatible land use can be estimated as follows. The Navy has spent over $500M in land purchases through the AICUZ program because of encroachment. A conservative estimate of off-post noise sensitive encroachment growth is 3 acres per day, DoD wide in Zone II and .03 acres per day in Zone III. Conservative estimates of noise-related property devaluation because of noise is 10% in Zone II and 50% in Zone III. This translates to the present value of about $750M at a 7.5% interest rate. Proven noise mitigation techniques are needed to avoid these costs.

Results from the physical model study will be used in computer program for predicting noise levels and in constructing noise contours. These programs, NOISEMAP and BNOISE, are used by the Army Environmental Hygiene Agency to map noise contours for Army installations as apart of the ICUZ and NEPA processes.

The combined human response model will develop improved impact assessment and control methodologies which will be able to deal with the multiple issues and questions raised concerning the current "universal" assessment methodology. This more robust and improved understanding of the issues will manifest itself as increased public acceptance of AICUZ/ICUZ studies and the noise portions of environmental impact analysis documents (EA's, EIS's) for future DoD operations. The results of the proposed program will provide more technically and legally defensible analyses of the effects of noise from DoD operations, less controversy surrounding the issues to be addressed, and less time required to implement changes in DoD operations.

9. Milestones/Accomplishments:

Turbulent Boundary Layer Effects on Sound Propagation.

1.	Use perturbations of measured profiles with the FFP	09/94
2.	Study shore range, range dependent media with the PE	09/94
3.	Develop boundary conditions for waves in random media	03/94
4.	Model and measure spatial and temporal coherence	09/95

Combined Effects Model for Human Response to Noise.

5. Develop plan for Blast/Sonic Boom Effects Studies	03/94
6. Preliminary consensus National Method for Combined Effects	09/95

A second complete draft of ANSI S12.9 Part 4 Quantities and Procedures for Description and Measurement of Environmental Sound -- Part 4. Assessment Methods has been completed and circulated to the working group. A revised draft is under development and will be circulated to the entire S12 committee for ballot.

Analysis of data gathered during July 95 at Naval Air Station Fallon is well underway. The purpose of the test performed at Fallon was to compare and contrast community response to blast noise and sonic boom. Current methodology combines these two categories of noise into one assessment. Laboratory-field studies of these two sounds in the same test is examining this methods of combination and will quantify any differences. The results will be modifications to the current model to better account for individual effects of these two sound sources.

10. Transition Plan:

Specific research results that result from this program will be incorporated into the USA AICUZ program and into the FIRE-system which is the primary tool used to mange noise and part RFMSS, the day-to-day Army training range management system. The Army Environmental Hygiene Agency will be the primary Army agency to implement technology transfer. In addition, the primary vehicle to transition the results of the proposed research program to the federal system is through FICON, which was established by direction of Congress for this purpose in FY92. The primary vehicle to transition to the private sector is through the American National Standards Institute (ANSI).

11. Funding: $(K)

	FY94	FY95	FY96	Total
SERDP	550	325	285	1,275

12. Performers:

The Department of Defense (DoD) has a coordinated noise program to develop noise mitigation and management technology. The Air Force is responsible for fixed wing aircraft noise and the Army is responsible for artillery and helicopter noise; the Navy relies on the other two services for noise mitigation technology.

The U.S. Army Construction Engineering Research Laboratories (USACERL) will function as the lead laboratory for the physical sound propagation model. Active basic research in this field is done by universities. Penn State, University of Illinois and University of Mississippi publish frequently on topics of this nature. Their work will be integrated into this program. Within the Army, work in sound propagation phenomena is also supported by the Army Tank command and

the Army Atmospheric Sciences Laboratory and the US Military Academy, with which we are currently participating with in joint field experiments and in data analysis and theoretical development.

For the Combined Effects Model for Human Response, performing organizations include the USA Construction Engineering Research Laboratories, USAF Armstrong Laboratory, the Federal Aviation Administration, the Department of Transportation, the National Park Service Ranger Activities Division, and NASA Langely Research Center. The U.S. Navy is not an active performer, since they do not actually perform any significant amount of research on the effects of noise on people, however they will participate in the planning and execution of this research. The US Army will be the lead organization.

13. Principal Investigators:

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14. Keywords:

Aircraft, Noise, Impulse Noise, Weapons Noise, Environmental Impact, Annoyance, TES, NEPA, ESA, Endangered, Threatened, Fast Field Program, Rifle Ranges, Small Arms, Noise Abatement, Noise Barriers, Shooting Noise.

SERDP FY96 PROJECT

1. **SERDP Thrust Areas:** Compliance

2. **Title:** Characterizing Open Burning/Open Detonation Emissions

3. **Agency:** U.S. Army

4. **Laboratory:** Dugway Proving Ground (DPG), Utah

5. **Project ID:** #247

6. **Problem Statement:**

The substantial amounts of energetic materials (propellants, explosives, and pyrotechnics (PEP)) accruing within the Department of Defense (DoD) have become an increasing burden on the military logistics system and subject of growing public concern. Storage facilities are now saturated by a demilitarization inventory exceeding 350,000 short tons and huge amounts of additional unwanted munitions are scheduled for retrograding to CONUS from overseas locations. Despite the critical need to reduce the demilitarization inventory, use of the only available process, OB/OD, has been sharply curtailed. Environmental regulators are demanding item-specific empirical data before granting OB/OD permits under subpart X of the Resource Conservation and Recovery Act (RCRA). These data are not available, and the system for obtaining them has not been fully developed. The Department of Energy (DOE) and defense contractors face a parallel situation at their installations which are accumulating substantial quantities of conventional unwanted energetic materials. Until new permits are granted or existing permits extended, the present dangerous situation will continue to worsen. Moreover, an already skeptical public may perceive that the failure of government agencies to obtain new permits as *prima facie* evidence that OB/OD activities are hazardous to their health and to the environment. The U.S. Environmental Protection Agency (USEPA) has begun closing OB/OD operations (e.g., Ellsworth Air Force Base, South Dakota) and citizens are demanding public hearings addressing risks from nearby OB/OD operations (e.g., Camp Edwards, Massachusetts, a field artillery training area for the Massachusetts Army National Guard).

Limited small-scale testing at DPG indicates that OB/OD-generated emissions of interest are so minute that they pose no hazard to health or the environment. However, the facilities, instruments, and procedures used during this previous testing cannot fully address the broad spectrum of conventional energetic materials awaiting disposal.

The goal of this project is to technologically expand testing facilities, instruments, and procedures so that they can be applied to current and projected disposal permitting-data needs. This includes designing new and larger BangBox testing chambers, characterizing emissions of complete munitions, and grouping munitions into emissions families so that future testing requirements can be abbreviated. During the course of this project, the testing system will be refined to the point where it is suitable for technology transfer to the commercial sector and can be marketed

worldwide. Research categories include basic and applied research. The project segment characterizing emissions is an exponential technical progression of a previously funded - and significantly smaller - pilot project.

7. Project Description:

The principal investigator (PI) will chair a technical advisory panel (TAP) which includes expert representatives from DoD, the U.S. Environmental Protection Agency (USEPA), DOE, the National Oceanographic and Atmospheric Administration (NOAA), and defense industries, contractors, and national experts. This panel will provide technical direction for this project and serve as a primary means for interagency coordination. Individual panel members will be selected by the PI.

This project will develop the system to sample, identify, and quantify emissions of environmental interest produced by the OB/OD of PEP end items in the DoD inventory, specialty explosives held by DOE, and PEP manufacturing wastes at DoD, DoD-contractor, and commercial sites. Testing will specifically target criteria gases, semivolatile organic compounds (SVOC), volatile organic compounds (VOC), and metals. The pollutant sampling and analysis systems used in the 1993 BangBox testing at DPG will be refined as the pollutants emitted from the various PEP are identified. New sampling and analysis methods (such as across-the-stack monitors) developed by EPA and the regulated community to measure toxic pollutants from stationary sources will be reviewed frequently to determine if one or more of these methods should be evaluated in the BangBox for use with OB and OD. Pollutant measurement systems evaluated in the BangBox found to be applicable to field and BangBox OB/OD activities will be prepared and standard operation procedures as soon as possible. As laboratory and statistical analyses become available, chemical and ammunition experts will group munitions into families by emissions and relate theoretical projections to empirical data so that testing requirements for the demilitarization inventory can be sharply reduced. Project personnel will use the best available technologies including, but not limited to, the enhanced BangBox test facility located at DPG, supercritical fluid chromatography/mass spectrometry, gas chromatography/mass spectrometry, inductively-coupled plasma mass spectrometry, evacuated and passivated 6-L stainless-steel canisters, and high-volume samplers. The PI, acting in concert with recommendations of the TAP, will direct technological enhancement of these facilities, instruments, and devices as needed. Anticipated detection of most SVOC and VOC emissions will be at the ppt and ng levels, respectively.

This objective also includes design and construction of specialized surface (5000 to 15,000 m^3 with internal support frames and suppressive shields) and ventilated subsurface chambers, the latter having the capability of accommodating the shock, heat, and shrapnel produced by detonating and burning complete munitions containing up to 45 kg of high explosive (HE) material. These specialized BangBoxes will provide the aggregate capability for expeditiously studying the effects of soil type and moisture content, munitions and propellant configuration (stacked/unstacked, buried/surface etc), presence or absence of combustion-promoting additives, quantity and type of munitions and propellants, and other variables on the pollutant profile and emission factors resulting from OB/OD operations. They will also provide the means of studying environmental dispersement of SVOCs and metals. If necessary, field OB/OD testing will be

conducted in a manner analogous to those executed at DPG in 1990/1991. An integrated database will collect and track data so that the pollution profiles of buried- or surface-detonated tested items can be compared and selected materials studied in more depth to identify the combustion dynamics and the kinetics of the principle chemical pathway associated with the production of pollutants and residues.

A panel of experts in risk assessment will prepare a guidance document listing the most reliable risk factors for the pollutants released from OB/OD activities and specifying how to use BangBox test results with these factors during the permitting process.

This is a low-risk project. All technologies exist, with only a few requiring moderate enhancement before they can be integrated into a complete testing system capable of fully characterizing emissions produced by the OB/OD of complete conventional energetic munitions and propellant end items.

Transferring technologies to the private sector for worldwide commercialization is designed into the project. Contractors will conduct most of the technical work, experts from the private sector will be on the TAP, and reports, when security is not a factor, will be in the public domain. Formation of cooperative agreements with private firms as authorized by the Technology Transfer Act will further facilitate transfer of the technology. Proprietary rights of technologies used in execution of this project will not be included in technology transfer agreements without the express consent of the owner(s).

This project directly supports the DoD objective of avoiding environmental injury during conduct of military-related operations.

The primary technical risk of this project is achieving normal combustion processes while also containing emissions during chamber-testing of munitions with an HE content exceeding 10 kg. The critical path encompasses the design and construction of the advanced BangBoxes described above. However, because the existing BangBox at DPG is adequate for testing of complete munitions containing up to 500 g of HE, initial experiments can be conducted with minimal startup time. Development of the risk assessment guidance document is dependent upon completion of OB/OD-related modeling efforts contained in a companion proposal. Testing of combustion-enhancing additives will be dependent upon results of the identifying and preliminary testing of such oxidizers as contained in a companion proposal.

8. Expected Payoff:

This project will provide the emissions data required by Federal and state regulators for evaluating applications for OB/OD permits under provisions of subpart X, RCRA. Existing OB/OD operations should continue and new permits issued if data indicates that risks to health and the environment are negligible. Because OB/OD destruction techniques are the fastest, safest, most understood, and least expensive means of disposing of conventional energetic materials, stockpiles of unwanted PEP items will be rapidly and inexpensively reduced. Funds

will not need to be allocated for developing special facilities or item-peculiar equipment for PEP items identified as being suitable for open-air destruction. Conversely, funds can be efficiently directed to development of alternate destruction methods for PEP items found not suitable for open-air destruction. Solid scientific data properly presented should allay existing concerns held by public about the safety of OB/OD disposal operations. Adaptation of the TOF mass spectrometer to BangBox testing of conventional energetic materials should result in a considerable reduction of laboratory assay costs.

9. Milestones/Accomplishments:

The TAP will meet on a quarterly basis unless convened earlier by the PI to address special situations.

1. First meeting of the TAP	07/94
2. Determination of feasibility of grouping munitions by emission families	07/95
3. Initiate design of one surface and one subsurface BangBox	07/94
4. First FTTA agreements in place	01/95
5. Initiate fabrication of BangBoxes	02/95
6. Draft report on testing and feasibility	09/95
7. Surface BangBox completed	11/95
8. New surface BangBox characterized	12/95
9. Subsurface BangBox completed	03/96
10. Initiate experimental testing of five items in new surface BangBox	12/95
11. Guidance on using risk factors for permit applications released	12/95
12. Subsurface BangBox characterized	04/96
13. Initiate experimental testing of five items in subsurface BangBox	05/96
14. Draft report of first new surface BangBox test	12/96
15. Draft report of first subsurface BangBox test	05/97

PEP materials tested in the BangBox: 1993 thru 1995 17 propellants, 12 explosives and 3 pyrotechnics materials commonly found in the demil inventory were tested. The 17 propellants and 3 pyrotechnics were burned and the 12 explosives detonated.

The results of testing to date, indicate emissions of interest are virtually nonexistent, BangBox data is being successfully used to keep OB/OD operational sites open, data is being used for permit application evaluation, and being successfully used to respond to NODs and NOVs.

10. Transition Plan:

The PI will distribute reports containing results of testing PEP items and manufacturing wastes to agencies having responsibility for obtaining subpart X permits and other interested government

agencies. These reports will be submitted to the Defense Technical Information Center where authorized members of the private sector may obtain them. The risk assessment guidance document will be distributed to USEPA and state regulatory agencies, and to DoD organizations involved in the permitting process.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	Total
SERDP	1,128	3,000	1,405	1,595	7,128

12. Performers:

This project is a collaborative effort. Government agencies involved in this project include the Department of Defense (DPG, Army Environmental Center plus other military departments as munitions are identified for testing), USEPA Atmospheric Research and Exposure Assessment Laboratory, NOAA, DOE (Sandia National Laboratories), and the private sector (Oregon Graduate Institute of Science and Technology, Alpine West Laboratories, Radian Corporation, ECO LC, Halliburton N.S., and others as TAP requirements expand). This project is part of the SERDP National Program for Open Burning/Open Detonation, for which the U.S. Army is the lead agency.

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14. Keywords:

OB/OD, BangBox, Disposal, RCRA, Munitions

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Measuring and Modeling for OB/OD Permitting

3. **Agency:** U.S. Environmental Protection Agency (USEPA)

4. **Laboratory:** National Exposure Research Laboratory

5. **Project ID:** #251

6. **Problem Statement:**

During the Cold War the United States of America, its allies and the former Soviet Union accumulated over 9,000,000 tons of conventional propellants, explosives (includes munitions) and pyrotechnic (PEP) materials. When the Cold War ended, these countries were faced with disposing of large inventories of unneeded or unserviceable PEP (energetic) materials in an environmentally sound manner. DoD alone has 400,000 tons awaiting the development of environmentally-safe disposal technologies and this "demil inventory" is growing at more than 40,000 tons per year.

From an environmental perspective the preferred methods for disposing of these materials are: (1) incineration; and (2) deactivation, recovery and recycling. Regrettably, most of the inventory is not amenable to these technologies for one or more of the following reasons. First, their composition is either unknown, unstable, obsolete or has degraded. Second, they cannot be disassembled safely. Third, the expense of developing a recovery/reuse technology for them cannot be justified based on the quantity in the demil inventory and/or the commercial value of the material that would be recovered. For many items in the demil inventory OB and OD are the techniques involve burning and detonating in an open area (OB/OD).

OB and OD are the techniques traditionally used for disposing of small quantities of unneeded or unserviceable PEP materials, because. of their technical simplicity, versatility and perhaps, most importantly, because of their low capital and operating cost. For example, OD of small quantities of PEP can be carried out in the U.S. at a cost of $200 to $1,200 per ton. In contrast, the equivalent cost for the existing recovery and reuse technologies range from $1,000 to $3,000 per ton (after the capital costs are amortized over 15 years).

The disposal of PEP materials by OB and OD is regulated under the Resource Recovery and Conservation Act (Subpart X of 40CFR264) To obtain a Subpart X permit, a facility must provide the following information to the regulatory agency. First, the identity and quantities of pollutants and debris that will be released per event and over time. Second, the magnitude of the blast waves and sound waves that will be generated. Third, a description of how these pollutants, debris, blast waves and sound waves will distribute in the environment. Fourth, the degree to which the health of humans and the environment will be endangered in the short term

(event basis) and over the lifetime of the OB and/or OD program.

One would expect that it would be easy to compile this information, since OB and OD have been used to dispose of unneeded or unserviceable PEP materials for over 150 years. But this is not the case, because OB and OD technologies have been developed almost exclusively through a "cut and try" approach, where the primary objective has been to ensure that the PEP material was completely destroyed and noise was controlled. There was little concern about the pollutants released and how they would disperse in the environment.

7. Project Description:

The objective of this project is to develop a mobile meteorological observation platform and air pollution dispersion model which can be used to predict the impact of open burning (OB) and open detonation (OD) of PEP materials on human health and surrounding ecosystems. It is divided into two tasks. The first task involves constructing a mobile meteorological observation platform (MAOP) for use at OB/OD sites. This system will include a 915 MHz wind profiling radar to obtain horizontal and vertical wind profiles from heights of 100 m above ground up to 3000 m over 100 m intervals; a radio acoustic sounding system (RASS) for the acquisition of virtual air temperature profiles from 100 m up to 1500 m over 100 m intervals; an acoustic sodar system to obtain high resolution (25 m) horizontal and vertical wind profiles in the first 500 m of the boundary layer; a lidar system to estimate mixed layer height; and at least one (and possibly more) 10 m tower system to obtain surface layer measurements of wind speed and direction, air temperature, relative humidity, solar radiation, barometric pressure, and turbulence variables such as fluxes of sensible heat and momentum. The MAOP will be designed in a modular fashion that will allow for future integration of more sensors if needed. This integrated system will provide real-time meteorological measurements which will help characterize the dispersive state of the atmosphere.

The second task is to develop an air pollution transport and dispersion model specifically designed to predict accurately how the emissions from OB/OD operations will disperse in the environment. The model will have the capability of being used at sites with either simple or complex terrain. The model will use the real-time data from the MAOP and from a database of expected pollution emission factors which will be produced by an OB/OD. The source of characterization work is being conducted by Dugway Proving Ground. Initial testing of the MAOP will be conducted at the Boulder Atmospheric Observatory (BAO) in Erie, Colorado where a 300 m tower outfitted with meteorological sensors will allow for side-by-side comparison of the data obtained from the profiling systems. The MAOP, along with the dispersion model loaded on a computer workstation, will be taken to several DOD facilities for extensive testing and evaluation in actual OB/OD activities.

8. Expected Payoff:

This project will provide DOD and DOE the tools to acquire the information needed to obtain a RCRA permit for OB/OD activities. Accomplished, it will be possible to use OB and OD to destroy large quantities (tons) of PEP materials at one time, on a routine basis while also

ensuring that the health of humans and ecosystems is protected fully at all times. This will allow DoD and DOE to reduce substantially the "demil inventory" and at a much lower cost per ton than those for the current technologies.

9. Milestones/Accomplishments:

1. First SERDP funds received	11/94
2. Expert panel workshop yields R&D plan	03/95
3. R&D plan presented at SERDP annual symposium	04/95
4. Design specifications for MAOP and model available	05/96
5. Meteorological equipment ordered	06/95
6. Paper presented at national AWMA meeting	06/95
7. Tower instruments received	10/95
8. Radian radar, Vaisala radar, RASS, sodar received	11/95
9. Testing of mobile met. platform (MAOP) initiated	01/96
10. Short-range model algorithms completed	01/96
11. Source characterization algorithms completed	03/96
12. Vaisala lidar compared with NOAA prototype lidar	04/96
13. Lidar system for use in MAOP selected	05/96
14. Algorithms for mixing layer depth completed	06/96
15. Short-range algorithms integrated into MAOP	07/96
16. Testing of MAOP at BAO completed	08/96
17. Field tests of MAOP at OB/OD facilities completed	10/97
18. Field tests of models completed	10/97

The R&D plan was developed at a workshop in 1995 at which experts in meteorology, dispersion modelling, and Subpart X permitting participated. (A NOAA Technical Report containing the workshop's discussions and explaining the scientific basis for the R&D plan is being published). The Plan was presented at the SERDP annual symposium in April 1995 and at the AWMA national meeting in June 1995. The equipment for the MAOP was received and the MAOP is being assembled. The algorithm for the short range model is now available. Papers describing progress made to date have been accepted for presentation at the 9th Joint Conference on the Applications of Air Pollution Metrology (Jan 1996; 2 papers) and at the 89th Annual National Meeting of the Air and Waste Management Association (June 1996).

10. Transition Plan:

This project will yield design and performance specifications for a mobile, ground-based meteorological measurement system applicable to OB/OD sites and recommendations on how to purchase, calibrate, operate and maintain it. It will also yield air pollution dispersion models with instructions on how to use them to obtain and maintain Subpart X permits. The PI will distribute the project's progress reports to agencies responsible for requesting or approving RCRA Subpart X permits and to other interested parties. The PI will publish continually reports in the peer-reviewed, open literature of the project's accomplishments. The field test to prove out the MAOP and Dispersion models will be done at active OB/OD sites to assist the users in becoming

knowledgeable about them.

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	TOTAL
SERDP	350	550	575	250	1,725

12. Performers:

This project is a cooperative effort involving the EPA, the National Oceanic and Atmospheric Administration's (NOAA) Environmental Technology Laboratory and Atmospheric Sciences Modeling Division (ASMD), and the US Army's Dugway Proving Ground.

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14. Keywords:

Open-air detonation; open-air burning; air pollutant dispersion modeling; OB; OD; meteorological measurement, profiler

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Encapsulation of Hazardous Ions in Smectite Clays

3. **Agency:** U.S. Department of Energy

4. **Laboratory:** Argonne National Laboratory (ANL)

5. **Project ID:** #315

6. **Problem Statement:**

The basic initiative under the SERDP Compliance thrust area seeks to develop new and novel materials for the control, treatment, and long term storage of hazardous metal ions, particularly those of toxic heavy metals and radionuclides.

The approach to be used is based on fundamental work on chemically stable organic monolayers at Harvard University and the Weizmann Institute. It involves the long-term encapsulation of ions in a new class of hydrophobic smectite clays, whose properties can be tailored to the specific chemical requirements of a particular hazardous species. Hazardous cations are initially introduced into the matrix of clay minerals, after which the system is encapsulated with hydrophobic agents.

Recent research in several laboratories has focused on the use of clays for environmental remediation. Current investigations have sought to develop ways to utilize these materials for the solution of problems in both organic and inorganic environmental contamination. This research combines the results of previous studies with our own expertise in surface modification of inorganic and polymeric substrates to create a new class of materials for use in environmental restoration.

Smectite clays consist of sheets of aluminosilicates which are separated by an interlayer that contains both inorganic cations, such as sodium, calcium and potassium. The cations in native clays can be easily replaced by other cations through aqueous ion-exchange processes. Therefore native clays can be readily used as filters for the removal of hazardous heavy metals and radionuclei.

For the remediation of organic materials, clays are traditionally rendered hydrophobic by treatment with quaternary ammonium cations that contain one long chain hydrocarbon tail. The resulting materials have a greater affinity for non-polar and modestly polar organic compounds. This method is, however, inappropriate for hydrophobic encapsulation of hazardous ions. Use of this process after a hazardous metal ion has been exchanged into the interlayer will only result in the release of the harmful species back into the environment. Clays which simultaneously bind hazardous cations and are hydrophobic are, however, of great interest. Such clays should exhibit

an increased resistance to leaching of the hazardous ions out of the interlayer by water. They would therefore require less stringent storage conditions once a hazardous material had been placed within them. Alternative methods, ones which do not rely on ion-exchange, are required to create these desired hydrophobic clays. The development of these methods, and the characterization and testing of the materials which result from them, is the subject of this project.

7. Project Description:

The research undertaken in this project seeks to replace the traditional cationic methods for creating hydrophobic clays with alterative general approaches which do not require the use of charged hydrophobic species. Specifically, we shall covalently bind alkylsilane groups ($CH_3(CH_2)_nSi$-) to the surface of the clay. This approach satisfies two objectives. First, it maximizes the capacity of the clay for the cation of interest. Since clays are electrically neutral, there is a maximum limit to the number of cations which can reside in the interlayer. By covalently binding the hydrophobic species to the surface, all of the cationic charge within the clay's interlayer is reserved for the cation whose encapsulation is desired. Consequently, the volume required by the storage medium for a given amount of hazardous waste will be minimized. Second, the use of a covalent bond to attach the hydrophobic medium to the clay eliminates the possibility that the modified clay can revert by ionic exchange back to the hydrophilic state. The covalent link between an alkyl chain and the surface of a clay, which is the basis of this proposal, is much more stable to the environment than the coulombic interaction present for the alternative quaternary ammonium species.

The method for creating a hydrophobic clay surface is derived from the work of S.R. Wasserman and G.M. Whitesides on monolayers of alkylsiloxanes. Like quaternary ammonium ions, the silanes change a hydrophilic surface into a hydrophobic one. Unlike the ammonium salts, however, the silanes do not carry a positive charge. They therefore can coexist within a clay along with hazardous cations. Both trichloro- ($RSiCL_3$) and trialkoxy-($RSi\ (OR')_3$) silanes form covalent bonds to the surface by reaction with surface hydroxyl groups. The resultant silicon-oxygen bonds are stable to strong acids, water, and organic solvents. Although this bond is susceptible to strong base, it resists attack under common environmental conditions. Previous work has demonstrated that dense monolayers containing from 2 to 18 atoms per alkyl chain form on surfaces of amorphous silicon oxide. Since clay minerals also possess surface -OH groups, the techniques developed for the creation of monolayers on silica should also be applicable to these aluminosilicates.

The protective layer on the clay will be polymeric. In addition to their reaction with surface -OH groups, the silanes react with surface water molecules, thereby forming silicon-oxygen bonds between adjacent alkylsilanes. The network of siloxane (-Si-O-Si-) bonds which is formed by this process constitutes a stable cross-linked structure that is held in place by bonds to the substrate and to adjacent silanes. This structure is of high molecular density. Well-formed monolayers of alkylsilanes prevent the penetration of even organic species into their structure. Therefore, this type of monolayer is should be an effective barrier to the entry of both polar an non-polar solvents into the interlayer of clay that contains a hazardous cation.

The presence of the cations in the interlayer of a clay represents a possible complication for the formation of the alkylsilane structures. The characterization of the cation in the hydrophobic medium will therefore be a major part of this project. In most cases, the positively charged species in a clay's interlayer are surrounded by solvating water molecules. During the encapsulation process, some of these water molecules may also react with the alkylsilanes. Such a process may further entrap the cation within the hydrophobic structure.
The nature of this project requires a multidisciplinary approach to the creation, characterization, and testing of this new class of clays. The initial focus of the research has been on the determination of the best experimental conditions for the creation of the hydrophobic clays. We have compared solution or vapor phase depositions for the silanes, as well as the material which result from the use of trichloro- vs. trimethoxysilanes as the precursor to the hydrophobic barriers.

The modified hydrophobic clays are being evaluated to determine how successfully the newly created barriers prevent the migration of the hazardous cations out of the interlayer. For these studies, environmental stresses, both chemical and physical, have been simulated. Several analytical techniques, including X-ray powder diffraction, X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), and nuclear magnetic resonance (NMR), have been used to characterize the structure and stability of the hydrophobic layer, as well as the changes which the lattice and interlayer of the clay undergo during the creation od the hydrophobic material. The results of these measurements serve to characterize how the clays withstand various stresses and how much material leaves the clay and enters surrounding fluids.

Although it is relatively easy to determine what proportion of the cation leach out of the clay, it is more difficult to quantify the environment of the cation within the interlayer. We have used X-ray absorption spectroscopy (XAS) to examine the local structure within 5 angstroms of the encapsulated cation. These studies have shown that trichlorosilane leave chloride ions within the clay. These ions interact with those of the stored transition metals. Because of the negative charge on the chlorine, this interaction mitigates the coulombic attraction which normally holds positive metal ions within the clay. As a result of these studies we have shifted our emphasis away from silanes which contain chloride.

Since much of the clay chemistry outlined in this proposal does not depend on the presence of radioactive materials in the clay lattice, most of the studies have used native, ion-exchanged, and silyated clays which contain representative non-radioactive elements. However, the structure of uranium within the hydrophobic clays is also being examined.

8. Expected Payoff:

The new and novel clay materials created during this study constitute the development of a new control technology for the treatment and disposal of hazardous wastes. They offer the possibility of improved long term storage for metallic cations whose re-entrance into the environment is undesirable. When native clays are used to filter waste species out of a medium, the resulting immobilized species still require stringent storage. Exposure of such clays to polar solvents which contain other ions can result in the re-exchange of the hazardous waste back into the fluid.

Rendering these clays hydrophobic without resorting to charged surfactants will result in materials that are much more resistant to typical environmental stresses. Therefore less rigorous isolation methods will be required for the long-term storage of these hazardous materials.

The modified clays will have a much different affinity for water than unmodified clays and other minerals. This difference should provide an effective means for separation of the hydrophobic materials from native minerals. Should the hydrophobic clays accidentally become remixed with other minerals, re-separation should be simple because of the drastically different flotation properties of the former.

The raw materials for this project, clays and organosilanes, are inexpensive. Clays are a major constituent of the earth, have many industrial uses, and have been proposed for environmental systems where cost minimization is an important consideration. Organosilanes have been used for over three decades for the creation of reverse-phased chromatographic column packings. They are also extremely inexpensive and readily available. Thus novel chemical concepts will be coupled in a rational way to provide a practical solution to a significant environmental problem.

9. Milestones/Accomplishments:

1. Preparation of hydrophobic smectite clays through the use of alkyltrichlorosilanes. 03/94
2. Preparation of hydrophilic and hydrophobic smectite clays with transition metals in the interlayer. 07/94
3. Characterization of the native and modified clays using powder diffraction, BET absorption measurements, X-ray photoelectron spectroscopy, flotation characteristics, and other physical techniques as appropriate. 09/94
4. Characterization of cations in hydrophobic clays by X-ray Absorption and Anomalous Small Angle X-ray Scattering. 09/95
5. Development of methods based on ion selective electrode to determine the amount of ions which leach out of the hydrophobic clays 02/96
6. Evaluation of efficacy of hydrophobic clays in resisting leaching 09/96

Hydrophobic clays have been prepared from both trichlorosilane and trialkoxysilane precursors. We have developed acid catalyzed systems for the formation of hydrophobic coatings from alkoxysilanes in non-polar solvents. These coatings have been applied both to native clays and to clays into which metal cation, including copper, nickel, lead, chromium, and uranium, have been introduced. Samples have remained hydrophobic even after storage in water for 18 months. Thermogravimetric analysis has shown that the coatings are stable under nitrogen to over 550 degrees C. X-ray absorption spectroscopy (XAS) has been successfully used to characterize the local structure with 5 angstroms of the stored cation. We have discovered that chlorine from the trichlorosilanes remains with the clay and associates directly with the stored cation. Studies suing anomalous small angle X-ray scattering indicate that the hydrophobic coatings do not cause a significant redistribution of the ions within the clay.

We are using ion selective electrodes to monitor the migration of stored ions from the

hydrophobic clays into water. Those clays modified with the alkoxysilanes apparently lead to a 3 to 10 fold improvement in keeping the encapsulated ion within the clay. As expected from the XAS results, those hydrophobic clays formed by reaction of the trichlorosilanes are not effective storage media for ions. This research was highlighted in the November 95 issue of Chemistry in Britain.

10. Transition Plan:

The technology developed under this proposal will be made available to potential users within the Department of Defense and Energy upon successful completion of the study. We shall collaborate with this and other appropriate industrial organizations as the scientific and technical breakthroughs develop.

11. Funding: $(K)

	FY94	FY95	FY96	Total
SERDP	380	200	200	780

12. Performers:

The lead organization for this project is the Chemistry Division of Argonne National Laboratory. The principal investigator is a member of the Chemistry Division at ANL. During the testing phase of this program, synchrotron experiments will be performed at the National Synchrotron Light Source and/or the Stanford Synchrotron Radiation Laboratory. The Analytical Chemistry Laboratory of ANL will provide basic analytical services. The analysis of the surface constitution of the modified clays by X-ray Photoelectron Spectroscopy will be performed by an external vender on a cost for service basis. In future stages of this investigation the personnel and the facilities of the Chemical Separation Science and Heavy Elements Coordination Chemistry groups of the Argonne Chemistry Division will help in the preparation and characterization of clays with tracers and other radioactive constituents.

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14. Keywords:

Encapsulation, Clays, Silanes, Monolayers, Multilayers, Cations

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Kinetics of Supercritical Water Oxidation

3. **Agency:** U.S. Department of Energy

4. **Laboratory:** Sandia National Laboratories (SNL)

5. **Project ID:** #364

6. **Problem Statement:**

Supercritical water oxidation (SCWO) is an emerging technology under development by government laboratories, universities, and private industry for the treatment of aqueous wastes. However, the current understanding of the rates and mechanisms of reactions in supercritical water is limited to a handful of empirical mechanisms for very simple chemicals. These mechanisms are of limited use in the formulation of predictive models of SCWO which will be needed in the future for the design and operation of large-scale waste processing equipment. It is also suited for treatment of waste materials best handled in water for environmental or safety reasons such as obsolete munitions, rocket motors, and chemical warfare agents. The process is performed at temperatures and pressures above the critical point of water (typically 450-650°C and 240 bar), and is applicable to waste streams containing 0-20 percent organics in water. The effluent from waste processing can be evaluated for compliance with applicable discharge regulations before release, ensuring protection of the environment.

An early patent for the process included data showing 99.99% destruction of many normal and halogenated hydrocarbons including tetrachloroethylene, DDT, and PCB. Since then, the number of organic and inorganic chemicals, as well as complex mixtures, tested by SCWO has grown considerably. However, the application of SCWO to most DoD and DOE waste treatment needs requires that the technology be advanced beyond its current level of development. These improvements will not be possible without better predictive models for the time, temperature, density, and concentration dependence of the oxidation process.

The current understanding of the rates and mechanisms of reactions in supercritical water is limited to a handful of empirical mechanisms for very simple chemicals. These mechanisms are of limited use in the formulation of a predictive model of SCWO. To be generally applicable and valuable as a design too, models must be based on elementary reaction steps or at least a detailed quantitative mechanistic description incorporating all the key fundamental reactions. Valuable progress is being made by several research teams but agreement between elementary models and experiment is only qualitative in most cases. In addition, there is a wide variation in experimental results and model predictions from different research efforts as a function of feed concentration, which emphasizes the need for closer collaboration among researchers.

A thorough understanding of operative chemical kinetics at the level of basic science is required to underpin applications of supercritical water oxidation technology. We propose a basic research project that investigates the currently uncertain chemical kinetics of SCWO. This project is a continuation and expansion of SERDP projects funded FY92 and FY93 title "Kinetic Mechanisms for Supercritical Water Oxidations" which established experimental capability and made initial measurements on fuel species and oxidation products in optically accessible supercritical water oxidation reactors. This project is improving our understanding of SCWO chemistry by directly measuring the time, temperature, and density dependencies of key reacting chemical species and improving the theoretical basis of reactions mechanistic models. This project extends the scope of the mechanistic models beyond the oxidation of simple single carbon organic systems to larger aromatic species and organic molecules containing nitrogen or chlorine.

7. Project Description:

The goal of this project is to produce predictive chemical reaction models to be used to aid the design and operation of large scale SCWO equipment. These engineering design models implicitly center on an accurate description of the chemistry of the key oxidation-resistant species. The insight and understanding needed to develop these models will be generated by coupling an extensive experimental program to a parallel theoretical effort producing quantitative mechanistic descriptions of the oxidation processes. These quantitative mechanisms will then be formalized into predictive computer models.

Actual wastes generated at DoD and DOE facilities are complicated formulations of large organic molecules and inorganic compounds such as paints, dyes, bonded explosives, solvents, and oils. However, work at Sandia and elsewhere has indicated that even at mild SCWO operating conditions, feeds of these complicated materials very rapidly convert to mixtures of simple chemicals. These chemicals are oxidation-resistant molecules such as methane and methanol, simple amines and nitrates, and phenol and other small aromatic ring species. Chlorinated systems represent an exceptionally important waste treatment problem for SCWO where hydrolysis and oxidation reactions are closely coupled. The oxidation rates of these molecules are the limiting processes for the complete destruction of complex feed materials.

This research project has several stages defined by the class of molecules to be studied and how these classes fit into a progression from simpler to more difficult chemical systems to model. Following methane and methanol, for which accurate mechanisms should be available from our current studies by late FY94, experiments and model development will be directed at the first two important classes of molecules: simple aromatics characterized by benzene, phenol, and benzoic acid, and chlorinated organics such as methylene chloride and trichloroethylene. The focus during FY95 and FY96 will be to generate accurate predictive oxidation models for engineering design use. Amines and nitrates, an important class of materials that relate to the treatment of energetic munitions and shipboard wastes such as black water, will be addressed in FY96-FY98 after the models for carbon/hydrogen/oxygen systems are in place.

This work continues the experimental approach from FY93-94 SERDP, extends measurements on key oxidant species, and expands the variety of experimental methods, primarily optical in

nature, that can be used to study reactions at SCWO conditions. In this project year we will begin to extend the elementary models developed for methane and methanol to more complicated species and continue to build the experimental data base. We will continue experiments on higher alcohols and chlorinated species, including propanols, phenol, anisole, and methylene chloride. The high density model for methane will be developed to properly account for the pressure dependence the FY94 experiments have revealed.

We will be directly collaborating with Princeton University on the chemistry of aromatic compounds and with MIT on the chlorinated and nitrogen containing species. We will work closely with Dr. K.E. Brezinsky and members of his research group at Princeton to develop the mechanistic description of phenol and toluene oxidation under SCWO conditions. We will collaborate with Prof. J.W. Tester and co-workers at MIT on experiments and model development for halogenated and nitrogen-containing systems.

The experimental portion of the research entails determining the concentration of reactants, stable intermediates, products, and in some cases radical intermediates associated with the oxidation of simple chemical in supercritical water. The time-temperature-concentration profiles that are measured provide the foundation for the mechanistic description of the many stages that even simple organic molecules pass through to completion of oxidation. Measurements of species concentration profiles of key intermediates are critical to developing chemical mechanisms. The experimental profiles of reactants and products provide test and verification of the quantitative capabilities of the predictive models.

Our work to date has proven spontaneous Raman spectroscopy to be a very useful method for measuring concentrations of a variety of chemical species in supercritical water. We have recorded strong signals from CH_4, CH_3OH, CO_2, CO, H_2, O_2, and N_2 at concentrations below 0.01 mole/liter. Data collected during FY93 on the oxidation of methane have contributed to the understanding of the temperature and concentration dependence of methane oxidation under SCWO conditions. This work demonstrates the power of optical methods for collecting the detailed experimental data that are necessary to completely describe chemical reactivity over wide range of pressure, temperature, and reactant feed concentrations. Measurement of trace species in FY95-FY97 will require application of more sensitive optical methods that will be adapted and applied as a part of this project. The primary experimental difficulty associated with this project is the level of detection sensitivity that will be achievable for reactive intermediates and products of partial oxidation. Consequently, the optical methods will be complemented by the analytical technique of direct sampling and off-line analysis.

The quantitative mechanism and model development will proceed in parallel with the experiments. Initially, predictions from existing elementary reaction mechanisms for low-density, high temperature processes will be compared to results from SCWO experiments. These comparisons will guide the design of new experiments. Subsequently, the results of the experiments will be used to improve the predictive performance of the models. We anticipate that additional steps involving peroxy chemistry will need to be added, as well as high-density corrections to unimolecular rate parameters.

We emphasize that the goal of this project is to produce predictive models for the oxidation of key species in supercritical water and not simply to illustrate the effectiveness of SCWO. The intention is that these models will guide the design of waste treatment equipment for specific DoD and DOE needs and that they will provide the necessary information to overcome critical design issues regarding equipment size, cost, or feed characteristics.

8. Expected Payoff:

SCWO is an emerging technology under development at several laboratories and in industry for the treatment of hazardous aqueous waste. Operation at densities two orders of magnitude greater than atmospheric gaseous combustion provides high reaction rates at moderate temperatures. The literature contains results of many studies of SCWO measuring destruction efficiencies for a variety of waste chemicals.

Some of this data can be used to generate empirical global kinetic rate expressions. The in situ measurements used in this project, particularly on unstable intermediates, can lead to valuable information for predictive model development. Data obtained in situ eliminates uncertainties associated with sampling and subsequent off-line analytical techniques. A better understanding of the fundamental reaction rates and the kinetic models this project develops will lead to models for reactor design, predictions of destruction efficiency, and methods for commercial system optimization.

9. Milestones/Accomplishments:

1.	Complete experimental studies and model development for methane and methanol at industrial process concentrations	06/95
2.	Identify hydrolysis role in overall role oxidation mechanism for chlorinated organics	10/95
3.	Complete phenol and higher aromatic experiments	03/96
4.	Complete mechanism for C,H,O organic oxidation	03/96
5.	Complete chlorinated organic oxidation experiments	03/96
6.	Initiate nitrogen-containing species experiments	01/96
7.	Complete predictive model for C,H,O organic oxidation	06/96
8.	Complete chlorinated species oxidation predictive model	12/96
9.	Complete nitrogen dioxide kinetics experiments, model nitrogen and nitrous oxide product distribution	03/97
10.	Complete amine kinetic experiments, model	10/98

Experimental and model development work on the oxidation of methane and methanol has been completed and has resulted in three literature publications. A fourth is in preparation The understanding of the oxidation process for these simple species is being extended to larger alcohols. Work on isopropanol and n-propanol, two species of significant applied interest in our work with Foster Wheeler Development Corp. for ARDEC and ARPA, has resulted in the identification of several key differences between these species. Two publications have been

submitted on this three-carbon system. Work at Princeton on phenol and anisole oxidation has demonstrated the key pyrolysis pathways for anisole. At MIT, the temperature ranges of oxidation and hydrolysis of methylene chloride have been identified under leveraged funding from the Army Research Office. Under this project, the details of the formation of formaldehyde at now being clarified.
The C1 elementary model now in place and is being extended to include chlorinated species.

10. Transition Plan:

Sandia National Laboratories is leading the development of technology for the U.S. Army ARDEC effort in SCWO. A contract is currently being negotiated for the fabrication of an approximately 100 ton/year unit. Results generated from this SERDP project will feed directly and immediately into improvements and modifications of production prototype equipment and larger scale systems designed to treat special munitions waste, pyrotechnics, and other military chemicals. The SCWO research team at SNL works in an environment of open information exchange with research and technology development efforts in universities, industry, and government labs sponsored by the Army Research Office, ARPA, the Naval Civil Engineering Laboratory, and the U.S. Air Force. In addition SNL directly participates in technology development projects in SCWO with ARPA and U.S. Army ARDEC. These two project involve close collaboration with Foster Wheeler Development Corp. and Aerojet Inc.

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	FY 98	TOTAL
SERDP	740	300	460	500	300	2,300

12. Performers:

The lead organization conducting this research project is Sandia National Laboratories, Combustion Research Department, Org. 8361. Mechanistic development for the aromatic molecules to be studied with FY94 and FY95 funding will be conducted in collaboration with Dr. K.E. Brezinsky and co-workers at Princeton University. Experiments and model development for simple chlorinated species will be conducted in collaboration with Prof. J.W. Tester and co-workers at MIT. In addition to mechanistic theoretical contributions and other collaborative research with Prof. Tester and Dr. Brezinsky, this project funds one research associate at MIT, as well as several extended visits to Sandia's Combustion Research Facility by MTI and Princeton researchers to conduct experimental work.

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14. Keywords:

Oxidation, Raman spectroscopy, Kinetics, Mechanisms, Supercritical Fluids, Research Modeling

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Waste Forms Based on Separations Media

3. **Agency:** U.S. Department of Energy

4. **Laboratory:** Pacific Northwest National Laboratory

5. **Project ID:** #360

6. **Problem Statement:**

A major mission of the DOE complex in general and the Hanford site in particular is the safe disposal of radioactive and mixed wastes. Disposal of such wastes from underground storage tanks will involve partitioning the waste into high-level and low-level components and converting those components into stable solids suitable for long-term storage.

DOE is currently planning to dispose of high-level wastes by converting the most hazardous materials into borosilicate glass. However, existing wastes such as tank sludge contain a range of species including chromates, phosphates, and aluminates which complicate production of borosilicate glass. Given the volume of sludge present (millions of gallons) and the high levels of dilution required to incorporate sludge into glass, it is estimated that direct conversion of existing tank wastes could generate up to 40,000 canisters of high-level waste glass. Not only would such volumes of glass greatly exceed the storage capacity of all known waste repositories, the costs of fabricating the glass alone ($1m/canister) could exceed $50 billion.

In order to minimize both waste volumes and costs, chemical separation procedures are under evaluation to concentrate most of the hazardous species into a small volume of high-level waste, allowing for disposal of the bulk of tank contents as low-level waste materials. An important class of chemical separations involves extracting hazardous species (or species which interfere with glass fabrication) using ion exchange procedures. Unfortunately, the separations process and the ultimate waste disposal process are often treated as separate entities. Commercial ion exchange materials are not tailor-made for hazardous waste disposal, and final waste forms are not being designed based on potential feed-streams generated from different separations scenarios. The focus of this proposal is to integrate separations and high-level waste form processing to optimize waste treatment technologies.

The active element in ion exchange is the sorbent material used to pack the ion exchange column. The sorbent material will ultimately be loaded with hazardous species such as radionuclides. Once the ion exchange column is loaded, two options exist to produce high-level wastes:

(1) The loaded ion exchanger could be used directly as the feed material for producing the final loaded high-level waste. Inorganic ion exchangers, in particular, can be (a) melted with other

oxides to form a glass or (b) calcined and sintered to form stable ceramics.

(2) Hazardous species could be eluted from the exchange column and converted into a pure product such as a metal salt. The pure compound would then be converted into a glass or ceramic waste.

Option 1 has the advantage that it minimizes the number of processing steps between ion exchange and final waste disposal. However, Option 1 requires that the ion exchanger itself be compatible with the final glass or ceramic waste form. Option 2 requires more processing, but it relaxes the requirement that the exchanger be compatible with the final waste solid. Option 2 might also generate less high-level waste.

Both options need to be evaluated to develop optimum processing schemes for treating hazardous tank wastes.

Separations and processing of waste at DOE sites has resulted in a variety of high level waste streams. In the past, separations have produced waste salts such as SrF2 and CsCl, and currently separations schemes are being considered for removal of Cs, Sr, I, Pu, and Tc from liquid waste streams at several DOE sites. In order to dispose of these various waste streams, an efficient process is needed that results in a stable, durable waste form that is resistant to attack by aqueous solutions. At present, the baseline conversion process involves dissolution of the various waste streams into borosilicate glass. However, many of the candidate separations materials, and the products separations processes, produce a waste streams which is either insoluble or incompatible with the current borosilicate glass formulations. In addition, the extent of dilution required to incorporate many to these wastes (such as phosphates or TiO2) into borosilicate glass results in prohibitive volumes of expensive borosilicate waste glass. Other options need to be considered for conversion of these problematic waste streams into a stable waste form. The primary objective of this task is to evaluate the feasibility of alternative waste conversion schemes for problem feeds generated as a result of separations. This research will impact needs in both the basic and applied research categories.

7. Project Description:

We propose to examine ion exchangers with potential for removing hazardous cationic and anionic species from tank wastes in the context of conversion into final waste forms. Existing candidate materials for Cs+ extraction include: the commercial zeolite IE-96, silicotitanates developed by Bob Dosch at Sandia National Labs, layered zirconium phosphates developed by Professor Abe Clearfield at Texas A&M (and by Allied Signal Corp.), and organic formaldehyde-resorcinol resins developed by Jane Bibler at Savannah River. Inorganic ion exchangers such as layered double hydroxides are under development by the Pacific Northwest Laboratory for removal of anionic species such as the pertechnitate ion. The overall program includes two components:

(1) Synthesis, and/or evaluation of exchangers thought to be effective at removal of species such as Cs+, Sr^2+, and TcO_4. Exchangers will be evaluated for chemical stability, selectivity and ion

exchange capacity, and compatibility with existing ion exchange processes. This evaluation will help determine the composition of the loaded exchanger and whether the exchanger is better suited to direct conversion into solid waste or elution to produce a more tractable feed.

(2) Evaluation and development of methods for converting potential feed-stocks produced via ion exchange into solid waste forms. A baseline activity would include determining whether the potential feed is compatible with borosilicate waste glass. However, alternate waste form options will also be explored.

A preliminary analysis of existing Cs+ exchangers illustrates some of the trade-offs associated with selecting materials to be optimized for both ion exchange and waste disposal processes. The zeolite IE-96 can be obtained as pellets suitable for ion exchange applications. IE-96 is also soluble in borosilicate glass. Unfortunately, IE-96 has a low selectivity for Cs+, resulting in low Cs+ loadings and high volumes of exchanged waste. Silicotitanates and zirconium phosphates have excellent selectivities, minimizing the total volume of exchanged high-level waste. Unfortunately, neither material can be used in ion exchange columns since both consist of nanometer-scale particles which can both clog and escape from columns. In addition, neither material is soluble in borosilicate glass. The organic resin has high Cs+ selectivity. However, the material is susceptible to radiation damage, requiring Cs+ elution and conversion before excess damage to the column occurs. As the above examples illustrate, most known exchangers have their own unique strengths and weaknesses for solving tank waste problems. The current program is aimed at identifying and mitigating the weaknesses of each of the above materials to provide the optimum solution to the Cs+ separation problem.

Work performed in the FY93 SERDP program on zirconium phosphate exchangers illustrates the approach we are following to explore processing and waste form options. While zirconium phosphate shows promise as a Cs+ exchanger, the loaded exchanger exhibits a low solubility in normal borosilicate glass due to its high phosphate content. With our SERDP project, we established a collaboration with Professor Delbert Day at the University of Missouri-Rolla to see whether he could develop an alternate host lattice for disposing of zirconium phosphate exchangers. On the SERDP project, Professor Day developed a family of iron phosphate glasses that can be loaded with zirconium phosphate. He was able to show that such a glass can tolerate Cs+ loadings at least as high as 30 wt,7o (compared with 5 wt% for borosilicate glass) and still exhibit a chemical durability to attack by aqueous solutions exceeding that of both borosilicate waste glass and window glass. The new phosphate glass has potential application for treating eluted cesium salts as well as zirconium phosphate exchangers. In fact, the glasses are under evaluation as a means of converting CsCl capsules (representing 1/3 of the total radioactive inventory on the Hanford site) into a stable glass waste form.

As noted above, several candidate inorganic ion exchangers, including silicotitanates, zirconium phosphates, and layered double hydroxides, have two major problems associated with them: 1) the nanoparticle exchangers must be consolidated or supported in order to be used in ion exchange column applications, and 2) the exchangers have a low solubility in the borosilicate waste glass host. Another activity underway in the SERDP project involves the development of porous glass supports to solve both of the above problems. Professor Day has developed two

methods for making porous glass supports for waste disposal applications: 1) leaching of phase separated borosilicate glasses, and 2) sol-gel synthesis of porous zirconium silicate glass. With such synthesis routes, glasses can be prepared with interconnected porosities ranging from micron diameters down to nanometer dimensions. Volume fractions of porosity can be as high as 50%. Such porous glasses could be an ideal support for nanoparticle ion exchangers, which could either be synthesized *in situ* via aqueous precipitation or loaded via colloid chemistry techniques. For certain exchange conditions, silane coupling agents could be used to attach the particles to the support. The supported ion exchanger could be configured as porous fibers or beads for use in ion exchange columns. Once loaded with radionuclides, loaded exchange columns could be hot pressed and/or melted to collapse the porosity in the glass. The resulting waste form would consist of ion exchange particles encapsulated (but not necessarily dissolved) in a highly durable solid glass host. Use of such a composite waste form could reduce waste volumes by as much as a factor of 50 for those exchangers exhibiting poor solubility in current borosilicate glasses. The above technology has yet to be demonstrated, but would be evaluated as part of the SERDP program.

8. Expected Payoff:

As stated above, the fabrication cost per waste glass canister is estimated at near $1M. Any contribution to the processing of hazardous waste that reduces the number of canisters is valuable. The processing issues addressed in this proposal clearly impact the number of waste canisters that must be fabricated. For example, it is estimated that the maximum allowed Ti content for borosilicate glass is 1 wt%. For a typical silicotitanate ion exchanger, this means that the volume of glass required to convert the exchanger into a solid waste for disposal would be roughly fifty times greater than the volume of the exchanger itself. Even if only 100 canister volumes of exchanger were sufficient to treat the 169 million-gallon tanks at Hanford, the process would generate 5,000 canisters of waste glass requiring disposal. However, if the silicotitanate can be directly converted into a ceramic or encapsulated in a porous glass, only 100-200 waste canisters would be produced for a potential savings to DOE of nearly $5 billion in processing costs alone. The phosphate glasses developed already in the program could have a similar impact on waste volumes if zirconium phosphates are the Cs+ exchangers of choice. An analysis of the different exchanger options might provide different solutions to DOE's waste processing problems that might emerge by consideration of the ion exchange step or glass fabrication step alone. For example, although zeolite exchangers are much less selective than silicotitanates for scavenging Cs+, the zeolites exhibit much higher solubilities in borosilicate glass. Although the zeolite exchanger would produce more solid waste after the exchange loading step, the net solid waste generated as glass canisters could potentially be less for the zeolite if both materials require disposal in borosilicate glass.

9. Milestones/Accomplishments:

FY96 Milestones	Date
1. Load Na-silicotitanate exchangers (CSTS) with Cs and determine temperature/phase properties.	12/95

2. Determine optimum iron phosphate waste forms for sludge dissolution. 01/96
3. Measure aqueous leach behavior of heat treated Cs and Na loaded CSTS. 03/96
4. Identify processing concerns for scale-up of iron phosphate glasses. 04/96
5. Fabricate glasses based on converted Cs+Na CSTS with minor additions of frit. 06/96
6. Measure to rate of corrosion of ceramic furnace liners for iron phosphate melter. 07/96
7. Measure leach resistance of frit-altered glasses. 08/96
8. Submit Final Report to SERDP 09/96

Work at PNL has concentrated on investigating alterative waste conversion options to borosilicate glass for the most promising ion exchange material; the crystalline silicotitanate exchanger (CST). In FY94, phase selection and durability information was acquired for compositions with the three major constituents of the silicotitanate ion exchanger, Cs2O-TiO2-SiO2. As a result of this work a new titanium-containing zeolite with a structure isomorphous to pollucite was discovered. Pollucite is known to be the best containment material for Cs, and, as expected, the Ti analog developed at PNL showed superior aqueous leach resistance. A patent has been filed on the new Tipollucite. More recent work has investigated the phase selection and durability of the actual ion exchanger (supplied by UOP and Sandia) loaded with Cs. When heat treated to temperatures comparable to the formation temperature of Tipollucite, these materials show excellent leach resistance and are a viable waste form material. Based on this work, we have shown that direct thermal conversion of a Cs-loaded ion exchanger is a cost effective alternative to dissolution in borosilicate glass. Direct thermal conversion has the potential to reduce the total number of high level waste borosilicate glass logs by 2000, which amounts to a savings of 2 billion dollars.

Researchers at University of Missouri-Rolla have developed iron phosphate glass compositions that can dissolve up to 20 times more zirconium phosphate ion exchanger than borosilicate glass and maintain durabilities comparable to borosilicate waste forms. After this early success their efforts turned to focus on three other problematic waste forms at the Hanford site that are only marginally soluble in borosilicate glass; CsCl, SrF2, and phosphate-rich tank sludge. As a result, they successfully produced iron phosphate glasses containing up to 28.5 wt% CsCl or 37.5 SrF2. These glasses show exceptional durability with dissolution rates 20 to 50 times less than the CVS-IS borosilicate glass. The physical properties of these waste forms indicate that these glasses are excellent candidates for disposing of the CsC and SrF2 capsules at Hanford, without any processing required prior to vitrification. Researchers at Missouri-Rolla have determined the density, thermal expansion, softening temperature, and dissolution rate of iron phosphate glasses containing five different simulated phosphate-rich waste sludges found at the Hanford site. Preliminary results indicate that some compositions can incorporate as much as 30 wt% sludge while maintaining durabilities similar to borosilicate glass. At these loading levels, there is a potential for a 90% reduction in the number of glass logs produced from processing phosphate-rich tank sludges which in turn provides an enormous reduction of the total processing cost.

10. Transition Plan:

The first objective of this project is to provide DOE with a technical basis for making decisions regarding both its separations and waste disposal options. Results from the program will then be implemented and incorporated into the actual tank clean-up procedures. If the program leads to the development of new exchangers, PNL will identify commercial vendors (such as Allied Signal) who will assume production of sufficient quantities to treat all tank wastes. If the major product of the program involves alternate waste forms, PNL will either work to transfer the waste form technology to existing DOE melt facilities, or will work with both DOE and commercial firms to develop alternate waste form fabrication facilities. If the major impact involves process integration, PNL will work closely with personnel assigned to cleanup of the Hanford tanks to see that optimum processes are implemented in a timely fashion.

11. Funding: $(K)

	FY94	FY95	FY96	Total
SERDP	200	100	200	500
DOE	180	220	200	760
TOTAL	380	320	400	1,260

12. Performers:

Organizations performing the work include Pacific Northwest Laboratory (DOE) and the University of Missouri-Rolla.

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14. Keywords:

Tank Wastes, Radionuclide Separations, Ion Exchange, Glass, Ceramics, Waste Disposal

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Shipboard Non-oily Wastewater Treatment System

3. **Agency:** U.S. Navy

4. **Laboratory:** Carderock Division, Naval Surface Warfare Center Annapolis

5. **Project ID:** #29

6. **Problem Statement:**

The goal of this project is to provide DoD vessels with the capability to operate in environmentally sensitive areas by meeting current and future national and international effluent discharge standards.

Provisions of the Clean Water Act control the overboard discharge of untreated blackwater (human waste) and graywater within the contiguous zone of the United States. Implementation of Annex IV of the MARPOL Protocol will regulate the discharge of blackwater and graywater from all ocean-going ships. No proven wastewater treatment technology exists today that will reliably meet both the secondary wastewater treatment standards (total suspended solids $\leq$ 30 mg/l, biochemical oxygen demand $\leq$ 30 mg/l, fecal coliform bacteria $\leq$ 14/100 ml and non-toxic) and the operating requirements of DoD vessels (highly reliable, maintainable, supportable, and safe).

DoD vessels today collect and hold only blackwater in collection, holding, and transfer (CHT) tanks for up to 12 hours, or until tank capacity is reached, while transiting the U.S. 3-mile contiguous zone. Graywater is discharged directly overboard. In the future, the 3 mile limit will probably be extended to 12 miles and graywater discharges may also be regulated. Other nations visited by U.S. naval vessels are also expected to impose more strict environmental laws. Ships that rely on holding tanks will be unable to comply.

This project falls into the technology demonstration category in which the feasibility and cost of combining technologies is demonstrated. A product of this research category is proof of the advantage to be gained through application of new technology.

This project is a continuation of an existing FY93 SERDP project. The FY93 effort involves a laboratory demonstration of complete treatment processes at the bench-scale and a subsequent trade-off analysis. That laboratory work will include pre- and posttreatment schemes coupled with membrane filtration to achieve consistent and acceptable effluent. Results from that evaluation will provide system performance data suitable for scale-up to the shipboard prototype.

7. Project Description:

This project will conduct a pier-side demonstration with al large scale 3 gal/min process to treat non-oily wastewater. The effluent will meet anticipated quality requirements of the US EPA and MARPOL Annex IV prior to discharge. The system is a membraned-based process, which employees membrane ultrafiltration (UF) as the "Keystone" technology that may be combined with nanofiltration (NF) as "post-treatment". Due to some uncertainty associated with future shipboard wastewater discharge regulations, major emphasis will be place on development of the "Keystone" ultrafiltration process; less emphasis will be placed on the nanofiltration post-treatment effort since it provides an effluent quality which potentially far exceeds the anticipated standards.

A 3 ga/min prototype has been successfully demonstrated pier-side with shipboard graywater; this unit will be modified to receive and treat non-oily wastewater. Treatment components of the prototype are not expected to change. The knowledge and experience gained from that demonstration will reduce the risks associated with handling and treating shipboard non-oily wastewater. The primary tasks include:

- Modify the prototype's configuration, as necessary, to receive non-oily wastewater and to meet effluent quality goals
  - Install prototype pier-side for non-oily wastewater demonstration
  - Conduct 4-month demonstration with non-oily wastewater

- Submit as the final product, a demonstration report and a design package (including P&ID, electrical, and layout drawings) that reflects the final configuration of the prototype used in the non-oily wastewater pier side demonstration

The risks associated with this project are: (1) the compatibility of UF membrane materials and actual shipboard wastewater as measured by continuous membrane service and membrane cleaning requirements; and (2) the strength of the shipboard wastewater and the impact of effluent quality.

A Navy 6.2 Project on membrane technology for graywater treatment identified ultrafiltration (UF) membranes as the central component to the treatment processes. This effort began in FY89 and will complete in FY94. Bench-scale and trial-scale test stands were fabricated for the evaluation of ceramic and polymeric membranes processing graywater under the 6.2 Exploratory Development Program, Block SC2A, P.E. 62233N, RM 33E60, Task F-8. This effort documented the inability of micro- and ultrafiltration membranes alone to treat graywater to meet secondary discharge standards for five day Biochemical oxygen demand (BOD_5). Additionally, it was found that polymeric tubular UF membranes provided the best combination of flux, permeate quality, system simplicity, and reliability in short-term evaluations in the laboratory.

The environmental compliance requirements which are met by this project are identified in the Tri-Service Environmental Quality Strategic Plan as: DoD Pillar 2, Thrust 2.B.2, Non-Oily Waste Emissions from Ships; Requirements 2.II.1.g Control and Management of Shipboard Non-Oily Waste.

8. Expected Payoff:

The development and demonstration of a prototype ensures compliance of every DoD vessel with all current and anticipated non-oily wastewater discharge regulations. Benefits include extended operational time in environmentally sensitive waters, ability to dock in domestic and foreign ports which do not have pier-side waste collection facilities and cost avoidance related to those facilities that do, and a decrease in space and weight on plumbing equipment installations to handle increased graywater holding time. Commercial shipping and the cruise line industry, which navigate within restricted zones for prolong periods of time, will also benefit from this process development.

9. Milestones/Accomplishments:

FY93 Funding

1. Complete contract for the design and fabrication of prototype non-oily wastewater treatment system	05/94
2. Complete trade-off analysis of all successful components and down-select	05/94
3. Complete laboratory evaluation of treatment process	07/94
4. Obligate funds for prototype development contract	07/94

FY94 Funding

5. Select Navy Site for Pier-side Demonstration	10/94
6. Complete Preliminary Drawings Package	10/94
7. Complete Review of Preliminary Drawing Package	11/94
8. Complete First Update of Drawing Package	12/94
9. Complete Critical Design Review of First Update	01/95
10. Complete Final Update of Drawing Package	02/95
11. Complete Pier-side Demonstration Test Plan	05/95
12. Complete Fabrication of Prototype	06/95
13. Obligate Funds for Analytical Contract	06/95
14. Complete Hydraulic Test of Prototype	06/95
15. Complete Proof-of-Concept Test	07/95
16. Deliver Prototype to Navy Site	07/95

FY95 Funding

17. Complete Pier-side Installation of Prototype	07/95
18. Complete System Debugging and Initial Testing	07/95

19. Complete Pier-side Demonstration of Prototype 11/95

FY96 Funding

20. Obtain Fleet Approval for Non-Oily Wastewater Demonstration 11/95
21. Complete Prototype Configuration Modification Drawings 12/95
22. Complete Review of Modification Drawings 01/96
23. Complete Update of Modification Drawings 01/96
24. Complete Test Plans 01/96
25. Complete Modification of Prototype 02/96
26. Complete Laboratory Evaluation of Prototype with Non-Oily Wastewater 02/96
27. Complete Pier-Side Installation of Prototype 03/96
28. Initiate Pier-Side Non-Oily Wastewater Demonstration 03/96
29. Complete Pier-Side Non-Oily Wastewater Demonstration 07/96
30. Complete Demonstration Report and Design Package 09/96

NSWCCD/A, with the contract support from MANTECH, completed 580 hours of pier-side testing along side a US Navy submarine tender on the 4000 Gal/Day shipboard prototype membrane system. No membrane cleaning was required to maintain the design production rate. Graywater feed characteristics such as BOD, COD, TSS, TKN, TDS, and fecal coliform were monitored; the system achieved a 70% reduction in BOD, a 99% reduction in TSS and 4 logs removal of fecal coliform bacteria.

NSWCCD/A completed two 200-hour laboratory evaluations with the "shell-in-tube" UF membrane module operating at a continuous 50-fold volume reduction of graywater; previous laboratory evaluations were conducted at a continuous 20-fold volume reduction of graywater. Membrane performance declined by 15-20% on average at the higher volume reduction as compared to the 20-fold volume reduction; statistical analysis of effluent quality is unavailable at this time.

NSWCCD/A conducted two ship checks of a DDG-51 Class destroyer. The purpose of ;the ship checks was to gather technical data on several suitable spaces for the future installation of a graywater treatment prototype. The information collected was used to prepare preliminary process and instrumentation diagrams and 3-D conceptual layout drawings.

10. Transition Plan:

Upon completion of a successful pier-side and shipboard demonstration, the prototype will be transitioned in FY97 to the Naval Sea Systems Command (SEA 03V) Advanced Development Program, P.E. 63721N. That program will design and fabricate engineering development models for evaluation and ultimate acquisition. Adequate industrial production capability currently exists for all components of the proposed treatment process.

11. Funding: $(K)

	FY94	FY95	FY96	Total
SERDP	700	250	450	1,400

12. Performers:

NSWCCD/Annapolis is the lead laboratory on this project. Dr. F. Cannon (Penn State Univ.) is scientific advisor to the project. NSXCCD/Philadelphia Code 631 (Pollution Abatement Branch) will assist in the installation of the pier-side prototype and coordinate with Naval Base and Fleet Activities. Mr. C.W. Davis, P.E. of Separation Technology, provides industrial applications support for membrane process design and operation. ManTech Advanced Technology Systems and GeoCenters, Machinery Technology Division (G-MTD) will provide engineering and fabrication support.

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14. Keywords:

Graywater, Blackwater, Ultrafiltration, Non-Oily Wastewater, Wastewater Treatment, Hybrid Wastewater Treatment Processes

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Compliance

2. **Title:** Evaluation of the Use of Waste Energetics as Supplemental Fuels

3. **Agency:** U.S. Army

4. **Laboratory:** U.S. Army Environmental Center (AEC)

5. **Project ID:** #524

6. **Problem Statement:**

The Army, as sole Department of Defense manager for explosives, is currently evaluating and developing safe, environmentally acceptable, alternative disposal and reuse technologies for it's stockpile of waste energetic materials. Energetic materials are propellants, explosives, and pyrotechnics and are commonly referred to as PEP. Unserviceable PEP materials are generated from the manufacture of PEP materials, assembly of munitions, and demilitarization of obsolete conventional munitions. It is estimated that approximately 2.5 million pounds of scrap and off-specification energetic are generated each year (1985 estimate). In addition there were an estimated 200,000 short tons of conventional munitions requiring demilitarization in 1990.

The disposal alternatives for these unserviceable PEP materials are open burning/open detonation (OB/OD) and incineration. OB/OD is the preferred method of disposal; however it's use requires a Resource Conservation recovery act (RCRA) Subpart X permit and due to environmental concerns, OB/OD is only allowed on a case by case basis. The Department of Defense (DoD) is seeking to qualify alternatives to OB/OD by 1995 and to adopt environmentally sound practices by the year 2000. Incineration of energetic materials is uneconomical. To safely burn these materials, energetic are mixed with up to 75% water to form an energetic material/water slurry. The water is required to prevent detonation propagation during the material handling and feed process. The addition of water increases the amount of fuel required to incinerate the energetic materials. Neither OB/OD takes advantage of the energy content of these materials.

The US Army Environmental Center (USAEC), formerly the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), began investigating the feasibility of reusing the energy content from waste energetic materials to produce steam and/or electricity in 1984. Since explosives are a major waste energetic material in the U.S. Army's inventory, the USAEC began investigating the potential of using TNT, RDX, and Composition B as a supplemental fuel.

7. **Project Description:**

The technical objective of this SERDP proposal is continue work on development of the supplemental fuel technology so that it is ready to be transitioned to the installations/users in order to deal with the burgeoning off-specification and obsolete energetic inventory. Continuing

to store these obsolete and unstable materials, while awaiting acceptable technical solutions, imposes great safety hazards. Disposal of waste solvated explosives as a supplemental fuel has been successfully demonstrated from the laboratory (1985), to the bench scale-studies (1988), to the Los-Alamos Pilot-Scale Test (1989), to the conduct of the Hawthorne Pilot-Scale Test (1991). Results of the first pilot scale demonstration at Los Alamos National Laboratory led to a state of-the-art pilot scale system being designed and constructed for mixing solvated explosives with fuel oil and firing the resulting mixture into a standard industrial boiler to generate steam. The test equipment was designed to meet strict safety standards involved in the handling explosives and volatile solvents. The major process equipment items in the pilot scale system are the explosives dissolving system, the fuel explosives blending tank, the boiler and steam vent system, and modifications shall be made and "as modified drawings" will be prepared (if necessary). A cost analysis shall then be performed and procurement/fabrication shall be prepared.

After conclusion of the Pilot-Test with explosives at the Naval Surface Warfare Center, Indian Head Division, (NSWC,IHDIV) and the pilot scale system is readied for the Pilot-Test with propellants (i.e., slurry nozzle identified in "Supplemental Fuels Development Support" contract is installed), a Pilot-Scale Test with propellants shall be initiated. Propellants investigated in this Pilot-Test shall be Otto fuel, Nitroguanidine, and Nitrocellulose. A final report shall be prepared at the conclusion of this testing as well as an operational manual and a video depicting system operation. Equipment modification shall be made and "as modified drawings" shall be prepared if necessary. A cost analysis shall then be performed and procurement/fabrication guidance shall be prepared.

Installations with burgeoning waste energetic inventories resulting from the manufacture of PEP materials, assembly of munitions, or demilitarization of obsolete conventional munitions who are interested in the technology shall be invited to witness both pilot tests with explosives and propellants. USAEC project office shall consult with project officers of USAEC's Installation Restoration Division to identify candidate installations for the conduct of a full scale demonstration should the technology prove to be both cost effective and successful. NSWC, IHDIV is also investigating the possibility of conducting the full scale demonstration at Indian Head, MD. USAEC technology transfer activities shall ensure maximum distribution of both cost analyses and procurement/fabrication guidance packages to installations and other users identified as interested in this technology.

8. Expected Payoff:

The future implementation of this technology could be a cost- effective disposal alternative to incineration and will become an alternative to OB/OD which soon may not be an option due to the environmental concerns associated with the process. Potential safety hazards may also be mitigated as the large stockpile of these obsolete munitions and scrap and off-specification materials can start to be utilized with this technology for a beneficial end use. This technology will not only benefit the DoD but commercial industry as well.

9. Milestones/Accomplishments:

1. Initiate Pilot Test on explosives at NSWC, IHDIV	09/94
2. Task award to Roy Weston	09/94
3. Technical report on NOx abatement technologies	02/95
4. Obtain/Install Equipment	02/95
5. Technical report on Slurry Nozzle Review/Study	03/95
6. Technical report on Data Gaps and Recommended Lab Testing	04/95
7. Site preparation activities complete	08/95
8. Recommended Lab testing results report	02/96
9. DDESB Approval	03/96
10. Approval from process review board	04/96
11. Baseline test with explosives completed	05/96
12. CEMS installation	06/96
13. CEMS certification	07/96
14. TNT test completed	08/96
15. Comp B test completed	10/96
16. Otto fuel test completed	11/96
17. Technical report on explosives testing	12/96
18. Full scale demo site selected	12/96
19. Nitroguanidine test complete	02/97
20. Nitrocellulose test complete	05/97
21. Technical report on propellants testing	07/97

All milestones listed above have been met and milestones in FY96 and FY97 are still on track in accordance with data projected.

10. Transition Plan:

DERA funding shall be used to fund a full scale demonstration at the installation selected in FY98/FY99. The transfer of the technology to the installation level is described in paragraph 7.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	Total
SERDP	800	185	495	415	1,780

12. Performers:

The USAEC and IHDIVNAVSURFWARCEN shall jointly develop and transition this technology. Roy F. Weston, under task order contract to USAEC is contributing in the development of the technology by identifying nitrous oxide abatement technologies for both pilot scale and full scale equipment, identifying acceptable slurry nozzles which can be used for firing propellants/fuel oil slurries in an industrial boiler, in conducting a comprehensive review of all laboratory and bench scale data pertaining to explosives and propellants-supplemented fuels in order to identify any

data gaps existing, and then to develop a test plan and execute testing to answer data gaps identified, and by providing consulting support to Indian Head, MD personnel during conduct of the demonstrations defined in this SERDP proposal. Sandia National Laboratories (SNL) as part of the Energetics Material Center (EMC) shall be a partner in this effort as they are investigating, under a separate SERDP proposal, tasks on the removal of energetic material and preparation for conversion which will support the material handling portion of a full scale demonstration. Sandia has also been provided $30K of FY95 funding to provide fuel characterization studies with both TNT and nitroguanidine in fuel oil and in toluene.

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14. Keywords:

Explosives, Propellants, Boiler, Supplemental Fuel, Pollution Prevention, Open Burning/Open Detonation

TABLE XIV
FY 1996 CONSERVATION PROJECTS

FY 1996 CONSERVATION PROJECTS	Funding $(K) FY96	ID Number	Page Number
Community Ecosytem - Management			
Terrain Modeling and Soil Erosion Simulation (A)	315	752	CS-3
Phased Array Ultrasonic Detection of Cultural Artifacts (A)	165	753	CS-6
Advanced Biotelemetry for Resource Management (A)	250	759	CS-9
Strategic Natural Resource Management Methodology (DOE/A)	750	373	CS-15
Multiple - Risk/Impact Assessment			
Predicting Environmental Impacts Resulting from Winter/Cold Climate Military Training (A)	500	1047	CS-22
Initial Framework for Assessing Military Training and Testing Impacts on Natural and Cultural Resources (A)	100	1048	CS-26
Species/Genetic - Management			
Threatened, Endangered and Sensitive Resources (A)	850	507	CS-31
Species/Genetic - Resource Characterization			
Integration of Radiotelemetry, Remote Sensing and GIS (DOE)	100	363	CS-37
Whale Monitoring Using IUSS (N/NOAA)	2,400	48	CS-42
Species/Genetic - Risk/Impact Assessment			
The Effects of Aircraft Overflights on Birds of Prey (AF)	350	89	CS-46
Genetic Diversity Monitoring in Plants and Wildlife (EPA)	190	246	CS-50
Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (EPA)	400	244	CS-55

TABLE XIV
FY 1996 CONSERVATION PROJECTS

	Funding $(K) FY96	ID Number	Page Number
Watershed/Landscape - Management			
Ecological Modeling for Military Land Use Decision Support (DOE/A)	340	758	CS-61
Conservation Total	6,710		

SERDP FY96 PROJECT

1. SERDP Thrust Area: Conservation

2. Title: Terrain Modeling and Soil Erosion Simulation

3. Agency: U.S. Army

4. Laboratory: Construction Engineering Research Laboratory

5. Project ID: #752

6. Problem Statement:

The objective of this basic research project is to develop methods and tools for prediction of spatial and temporal distribution of runoff, soil erosion, and sediment deposition within watersheds. Soil erosion and consequent siltation of waterways have long been major environmental concerns on military installations. Most existing approaches rely on lumped-parameter semi-empirical relationships developed for agricultural fields. Such approaches are unable to provide consistent, accurate results for watershed-scale runoff and erosion processes. Another primary limiting factor is the inability to accurately represent the terrain in a digital form necessary for high resolution watershed-scale erosion and sediment transport modeling. The development of new-generation technical tools to model distributed surface erosion and runoff in complex terrains is a necessity. Such tools will provide a basis for predicting the environmental impacts of military-related activities and for the optimization of land rehabilitation programs for installations.

7. Project Description:

The research effort will incorporate the following parallel thrusts: a) Further enhancements of spline interpolation methods to support terrain modeling and processing of field measurements; b) Further development of the unit stream power based modeling of erosion and deposition potential; c) Simulation of rainfall-runoff processes through the application of two-dimensional finite difference technique with the addition of sediment transport routines; d) Development of a vehicle-soil-climate interaction model based on field measurements of soil and hydrologic parameters as consequences of various types and intensities of military vehicular traffic; e) Collection of in-stream sediment concentrations of validation of the proposed models; f) Development of new visualization techniques supporting the design and communication of models of dynamic processes, such as erosion and sediment transport.

The project is focused on the development of computer-based models that will support the determination of the impact of military activities on natural resources and will assist in maximizing availability of military lands with minimal impact to natural resources, especially to soil and vegetation.

8. Expected Payoff:

This project will improve the capability to generate accurate digital elevation models and perform topographic analyses for various terrain related applications. There will be improved capability to estimate erosion/deposition potential as an input for choosing the optimal land use management and rehabilitation programs. Modeling of erosion and deposition will assist land managers and trainers in optimizing the training schedules, delineating training areas, and monitoring changes over time. The models will also assist in maximizing availability of military lands with minimal impact to natural resources, especially to soil and vegetation. The overall net result of this research will be improved land management and reduced land maintenance costs.

9. Milestones/Accomplishments:

1.	Interpolation enhancements (floats)	09/95
2.	Scripting for dynamic visualization	09/95
3.	Erosion/deposition model enhancements (divergence)	12/95
4.	Initiation of small basin monitoring	01/96
5.	Implementation of multidimensional dynamic visualization	03/96
6.	Validation of enhanced rainfall-runoff model	09/96
7.	Field validation of erosion/deposition model	10/96
8.	Draft journal article on erosion/deposition model	11/96
9.	Incorporation of sediment control practices into models	09/97
10.	Interactive decision support system for simulation of runoff and erosion processes supporting optimal land use management	09/98

All milestone listed for 1995 have been accomplished on schedule. A generalized spline interpolation methods was developed to support accurate, high resolution terrain modeling from digital elevation data. This significantly improves the capability to compute and use digital elevation models and topographic analysis for various terrain related applications including erosion and runoff modeling. Information, examples and demonstrations of the multivariate spline interpolations programs are available on the World Wide Web at http://www.cecer.army.mil/grass/viz/VIZ.html. Based on a very high resolution, high quality data set from an experimental farm in Germany, we have illustrated the high level of accuracy in predicting erosion and deposition.

10. Transition Plan:

Scientific papers in peer reviewed journals will be published. Improved programs will be released with updates of GRASS geographic information system . The information will be disseminated via the World Wide Web. Programs developed under this effort will be incorporated into land management decision support systems.

11. Funding: $(K)

SERDP	FY94	FY95	FY96	FY97	FY98	TOTAL
	600	195	315	700	300	2,110

12. Performers:

Land Management Laboratory at USACERL, Geotechnical Laboratory and Hydraulics Laboratory at USAEWES, the University of Illinois, Texas A&M University

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14. Keywords:

Terrain Modeling, Soil Erosion, Watersheds, Runoff, Sediment, Impacts

SERDP FY96 PROJECT

1. SERDP Thrust Area: Conservation

2. Title: Phased Array Ultrasonic Detection of Artifacts

3. Agency: U.S.Army

4. Laboratory: Construction Engineering Research Laboratories (CERL)

5. Project ID: #753

6. Problem Statement:

The goal of this work is to develop a ground penetrating acoustic probe using the phased array and/or synthetic aperture technology for the sub-surface detection and imaging of artifacts.

Currently, the reliability associated with the detection and location of artifacts is minimal. Often, valuable finds are missed only to be found during construction, causing delays and increased costs. Sound waves exhibit the non-destructive capability of being transmitted into the ground to probe beneath the surface by being reflected off of mediums of differing relative density (i.e. bone, ceramic, stone, glass).

7. Project Description:

Acoustic techniques are in routine use for medical, engineering, and oil exploration applications. Three-dimensional or two-dimensional (tomographic) imaging of everything from human fetuses to oil fields are now commonplace. The objective of this work is to develop and demonstrate a phased array of acoustic transducers which can accurately image subsurface features of differing densities. For example, by analyzing the signal strength returned within specific time windows, precise regions can be examined. By varying these windows, the whole volume can be examined while excluding most interference reflections. Through computer imaging and enhancement, the location of possible artifacts can be identified along with information about their shape and dimension.

The demonstration phase of this work will begin at the Controlled Archeological Test Site (CATS) planned for construction at USACERL in the Spring of 1996. Next, known archeological sites will be used for verification and characterization of operational parameters. The capability for site assessment will be verified by "ground truthing" where conventional archeological excavation techniques are used. These results will then be compared to those obtained by the phased array.

8. Expected Payoff:

This work will develop the capability to more cost effectively assess archeological site for eligibility to the National Registry of Historic Place (E.O. 11593) and better use limited assessment resources. In addition, the expense associated with compliance with the Native American Grave Protection and Repatriation Act (NAGPRA) will be reduced. As well at construction sites unanticipated discovery will be reduced and delays avoided. Potential uses also exist in the areas of land mine and unexploded ordnance detection/location, contaminated dump site assessment and utility location.

9. Milestones/Accomplishments:

1.	Survey commercial systems and services	09/94
2.	Build test bed for transducer and imaging software testing	09/94
3.	Complete characterization of acoustic properties of soils and sub-soils	09/95
4.	Build transducer/detector array	06/96
5.	Wire computer interface	06/96
6.	Develop control and imaging software	03/97
7.	Test at Controlled Archeological Test Site (CATS)	07/97
8.	Demonstration of technology	06/98
9.	Report on findings	09/98

The acoustic properties of six representative soils have now been characterized in a controlled and reproducible manner. Applied engineering research to minimize input signal loss and reliably detect reflection is nearing completion. Initial design and signal processing work is under way in association with the Beckman Institute for Advanced Science and Technology at the University of Illinois. A supporting theoretical study has been completed at the University of Arizona and the publication "Topics in Wave Propagation in a Random Medium" is being prepared for publication. Initial discussions are under way concerning the loan of a phased array from the Penn State Applied Research Laboratory, originally developed for the Navy. Though not optimized for the intended application, valuable experience will be gained by being able to compare and optimize various approaches to acoustic signal processing.

10. Transition Plan:

The technology will be transitioned to DoD through the Tri-Services Cultural Resource Center. In the commercial sector there has been interest expressed by Vista Research, Inc., for commercialization (utility location). Other potential commercial partners will also be identified.

11. Funding: $(K)

SERDP	FY94	FY95	FY96	FY97	TOTAL
	261	120	165	340	811

12. Performers:

US Army Construction Engineering Research Laboratories, Champaign, IL, Tri-Service Cultural Resource Center, Champaign, IL, University of Illinois, Urbana, IL, University of Arizona, and the Missouri River Division of the Corps of Engineers.

13. Principal Investigator:

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14. Keywords:

Acoustic, Sonic, Cultural Resources, Probe, Ultrasound, Array, Artifacts, Transducer, Sub-surface Location, Ground Penetrating Acoustics, Synthetic Aperture

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Advanced Biotelemetry for Resource Management

3. **Agency:** U.S Army

4. **Laboratory:** USAE Waterways Experiment Station

5. **Project ID:** #759

6. **Problem Statement:**

The federal, state, and DoD requirements for research, management, and conservation of natural resources are costly and can impact and disrupt military missions. The object of this proposal is to develop and implement sophisticated remote sensing biotelemetry technology and to develop methodologies to study wildlife on military installations while minimizing disruption to military activities.

The use of advanced technology proposed here will address two difficulties that plague effective research and management of special status species on military land: 1) rare or elusive organisms are difficult to find and study; and, 2) human activity involved in conventional study of these organisms can interfere with military activities.

Threatened and endangered species protection has precluded certain military operations on DoD installations and other federal and state lands. The projected cost in both fiscal and personnel resources for studying threatened and endangered species is significant.

Furthermore, field study activities often place natural resource personnel in situations that interfere with military activities and sometimes may require personnel to enter hazardous impact areas. To address these problems, biotelemetry and specialized survey methods can be used to remotely acquire large quantities of data for long-term studies of wildlife. Biotelemetry can be especially effective for studying threatened and endangered species and migratory organisms that are often indicators of environmental conditions.

This advanced technology can also be useful in addressing other DoD environmental requirements, such as managing for biodiversity and/or neotropical migrants, and monitoring and controlling of environmental contaminants. The application of the proposed technology will streamline data collection and will reduce the personnel investment and interference in the field while demonstrating leadership in DoD natural resource management responsibilities. Our proposal will build on a previously funded DoD technology development project that addressed several protected species while developing natural resource management methodologies and technology. The proposal encompasses basic and applied research, technology demonstration, and technology transfer as specified below:

Basic Research:

- Development of environmental sensors and integration with biotelemetry
- Development of enhanced survey and monitoring methods
- Integration of data from remote sensing and surveys with Geographic Information System (GIS) databases for installation resources management

Applied Research:

- Implementation of the technology and methodologies from basic research to study the effects of military training and other relevant land use activities on natural resources

Technology Demonstration:

- Demonstration of resource management planning on selected DoD installations integrating the enhanced technology and methodologies

Technology Transfer:

- Transfer technology and methodologies to U.S. Department of Interior's (DOI) Bureau of Land Management (BLM) and National Biological Survey (NBS) for use in natural resource management

7. Project Description:

Our goal is to provide DoD/DOE managers with more effective and efficient ways to meet their environmental objectives. The critical path for the implementation of our proposal requires parallel development in: 1) field methodologies and biometrics; 2) electronics and applied physics; and 3) natural resource research and management. We plan to work with selected installations and their land managers to identify their needs in addressing natural resource problems and then develop innovative methods and technologies required to address their needs. We will include the field testing methods and techniques and the incorporation of them into the natural resource research, planning and management program.

This development and integration of new environmental sensors with conventional and global positioning systems will be carried out in three phases. Phase I will involve the integration of motion, temperature, altitude, and light sensors with globally positioned Argos-Tiros Platform Transmitting Terminals (PTT). Phase II will involve the development of miniature acoustic sensors for use with conventional positioning and tracking systems. Phase III will be the integration of GPS and acoustic sensors with the Argos-Tiros PTTs.

Biotelemetry will be used as an animal marking technique in developing new survey and monitoring methods (i.e., mark-recapture). Also, biotelemetry will be used to identify the spatial-temporal use of areas and habitats of interest (e.g., training areas), and to help identify sources of disturbances and contamination. Biotelemetry and survey methods will also be used in research

on potential influence of selected human activities on wildlife. The proposed work will be integrated with the existing program to maximize exchange of information and minimize duplication. The current program involves several DoD entities: National Guard Bureau (NGB), US Army Construction Engineering Research Laboratories (CERL), and US Army Edgewood Research, Development and Engineering Center (ERDEC); several US Department of Interior agencies; Fish and Wildlife Service (USFWS), National Park Service (NPS), and the National Biological Survey (NBS), Bureau of Land Management (BLM), and several academic institutions: Johns Hopkins University Applied Physics Laboratory (JHUAPL), Virginia Polytechnic Institute and State University (VPI), and Boise State University ID. By working with NBS's Division of Information and Technology Transfer and CERL, we will maximize our opportunity for technology and methods transfer to other natural resource and conservation efforts ongoing throughout the country.

Potential technical difficulties include: 1) achieving statistical robustness for the study of uncommon organisms; 2) additional miniaturization of telemetry technology for application to small animals; and 3) sensor range and sensitivity applicable to environmental monitoring.

8. Expected Payoff:

The primary benefits of our proposal are cost savings for DoD resource managers, enhanced research and management capabilities, and new technologies for a variety of users.

Cost savings to the military accrue in several ways. First, application of advanced methods and techniques will allow for more effective accomplishment of the study of special status species. Second, application of these methods and techniques will require fewer personnel resources than in the past. Third, fewer persons in the field for shorter periods of time will reduce the interference with military activities.

In addition to more effectively meeting DoD's obligations for natural resource conservation, the technologies we develop will have applications to other military missions. For example, miniaturized telemetry devices can be applied to positioning military assets (e.g., covert devices, search and rescue activities, and "lost" items). Furthermore, sensors developed for monitoring an animal's environment are equally applicable to sampling the environment of troops or other military assets.

These methods will also be applied to basic research on the effects of the military and other anthropogenic stressors on natural resources. The data acquired can be directly applied to resource management planning that is "proactive", whereby we can avoid creating problems and causing species to become threatened or endangered. By preventing disturbance of certain sensitive habitats, DoD and DOE can avoid the expensive, time-consuming, and disruptive responses necessary to manage and mitigate for environmental problems. This approach will also promote better biodiversity management.

Currently, DoD and DOE share with DOI, the Department of Agriculture, and the Department of Commerce many common concerns and responsibilities for the environment. Furthermore,

DoD and DOI are actively involved in the development of international programs to address environmental concerns resulting from their activities and those similar agencies in other nations (e.g., Ministry of Defense, Russian Federation). Our methods and technology are broadly applicable regardless of the user community. This broad application is, in fact, required because the world recognizes the global links among natural systems. These links include such diverse pathways as the migration of birds to and from military lands of many countries, and the circulation of contaminants across political boundaries through the atmosphere and waters of the world. Furthermore, our technology will be available for testing hypotheses, investigating alternative strategies, and monitoring for the predicted effects of global warming.

9. Milestones/Accomplishments:

1. Continue miniaturization and integration of acoustic sensor with conventional/PTT systems	02/96
2. Continue the integration of GPS capability with the Argos PTT	02/96
3. Continue program with DOI on integration of data bases with GIS	03/96
4. Interim reports on sensor development (acoustical sensors)	12/95
5. Interim report on GPS function integration with PTT	12/95
6. Field test integrated GPS with PTT	07/96
7. Field test integrated acoustical sensors with conventional telemetry systems	06/96
8. Final report on laboratory development effort pertaining to integration of miniature acoustical sensors	09/96
9. Final report on integration of GPS with the Argos PTT	10/96
10. Final report of field testing of GPS/Argos PTT.	10/96

Progress on the integration of an acoustical sensor with a conventional telemetry system is progressing at the Johns Hopkins University, Applied Physics Laboratory. Meetings have been held with the Air Force in order to integrate the two efforts on the development of a telemetry device to collect and transmit acoustical information gathered in the microenvironment at the surface of free ranging animals and birds. The effort to integrate a Global Positioning receiver with an Argos Platform Transmitter Terminal is underway with Microwave Telemetry Inc. Several prototype transmitters will be developed within the next six months for test and evaluation. Presently GPS units are being evaluated for interface with the Microwave NANO PTT 100 which has been used on over 20 species of birds in the past two years. Prototypes are under design to weigh not more than 200 grams for test and evaluation on several large bodied avian species in the spring and summer of 1996.

The National Biological Survey is presently collating data from the Argos system and assisting in the integration of satellite telemetry data with on line Geographic Information Systems for the demonstration of the use of the technology to manage natural resources for the Department of Defense. Although some of this work is being conducted under the Legacy program, this organization will be managing the data base for the SERDP program as our telemetry systems come on line in the next six to twelve months.

10. Transition Plan:

The technical development and integration of new environmental sensors with global/conventional positioning systems for natural resource management and wildlife research will be managed by ERDEC and performed by the JHUAPL working in union with the private sector. In the past, our US Army program, "Bird Borne" (performed by JHUAPL), proved to be a cost effective mechanism for development and rapid transition of technology to industry. Our early research and development in military application resulted in a new generation of miniature PTTs (28gm) which are now available from private industry.

Prototype systems from all three phases of development will be transitioned to several field programs for test and evaluation of performance. These field efforts will be managed by NBS and DoD. The NBS will provide oversight for the development of scientific protocols for the use of the technology for application in select military and DOI natural resource programs. These applications will be with the Idaho Army National Guard (IANG), and several wildlife research efforts conducted through the USFWS, BLM, and NPS. Evaluation of the technology, and synthesis and analysis of results will be carried out by the elements of the NBS and individual commands/installations and agencies. Integration of developed databases derived from the use of this technology on several of the fielded programs will be integrated into a GIS capability which is currently under development jointly by CERL, NBS, and IANG.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	300	270	250	820

12. Performers:

The principal performer in this research effort will be the scientists at ERDEC. These scientists will coordinate and, when possible, partner activities with Tri-Service installation personnel, with land management agencies such as USFWS, USDA FS, USDA SCS, BLM, and BUREC, with academia, and with the Nature Conservancy and other conservation organizations.

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14. Keywords:

Landscape Planning, Watershed Management, Ecosystem Management, Ecosystem Functions, Integrated Resources Management, Cultural Resources, Natural Resources.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Strategic Natural Resource Management Methodology

3. **Agency:** U.S. Department of Energy

4. **Laboratory:** Argonne National Laboratory (ANL)

5. **Project ID:** #373

6. **Problem Statement:**

Argonne National Laboratory (ANL), in conjunction with the U.S. Army Corps of Engineers, Construction Engineering Research Laboratories (USACERL), is creating a Strategic Natural Resources Management (SNRM) methodology and developing a decision-support system that will meet planning needs for biological conservation and resource management on military installations. This system will also allow users to evaluate several alternative land management strategies and choose among them on the basis of values and objective judged to be appropriate for their specific context. Since these trade-offs are complex, it is of critical importance to define a value trade-off model that quantifies the outcomes of different activities (as represented by the maps showing the status of the land), so that better and worse outcomes can be distinguished. Such an approach will structure the definition and analysis of values associated with land management and training activities to support US Department of Defense (DoD) requirements and needs in a cost effective and efficient manner.

This proposed computer decision-support system, called the Integrated Dynamic Landscape Analysis and Modeling System (IDLAMS), will:

1) Allow land-use conflicts to be identified and evaluated,
2) Identify high-value alternatives,
3) Enhance environmental compliance,
4) Determine solutions to long-term land stewardship issues, and
5) Reduce DoD costs and support the overall military mission

This approach will quickly provide pertinent information for determining, evaluating, and resolving natural resource/land use conflicts as well as for long-term planning and management of these natural and cultural resources. This project's scientific approach and the resulting IDLAMS system will enable resource managers to predict the effects of land management actions, both spatially and temporally. The project offers a planning framework and a technology that will be transferred to installation site managers by providing pertinent resource information and a set of computer tools linked to their existing geographic information systems (GIS).

The project offers a technological approach that will enable resource managers responsible for public lands to identify and analyze competing and complementary land uses and to incorporate least-cost, optimization, and "what if" scenarios into their decision-making. The initial emphasis focuses on Army installations; however, the technology will be a tool relevant to the needs of the Navy and Air Force, the Department of Energy, the Bureau of Land Management, the National Park Service, and other federal and state land managing agencies. As such, IDLAMS will be a dual-use technology with the potential for leveraging the Department of Defense funds with those of other agencies for future enhancements and technology transfer.

Background work underpinning this proposal was conducted at Fort Riley, Kansas, where ANL developed a dynamic community landscape model that links the installation's training mission with the protection of its natural resources. This model is being integrated with a value-based decision analysis approach and geographic information system (GIS) to create a user-friendly interface to be used by the installation's natural resources planning staff. The Fort Riley methodology is being expanded and generalized to meet the major needs of biological conservation and resource management on military installations and Department of Energy sites.

Relevant USACERL projects have been funded through the Legacy Resource Management Program to develop pilot computer technologies to assist in integrated natural and cultural resource planning and management on military installations. These USACERL projects include XCRIS, an X-windows-based Cultural Resource Information System, and PRISM (Planning and Resource Integration Stewardship Modules). These efforts have linked computer tools, including a GIS, a relational database management system, and graphic user-interfaces using easy-to-use information access and decision support technology. Initial resource "modules" include cultural resources and historic preservation, forestry, endangered species (specifically for the red cockaded woodpecker), and watershed management and erosion control. The IDLAMS methodology will build upon these efforts by developing a quantitative approach to evaluating land-use alternatives and long-term resource management scenarios.

7. Project Description:

Based on DoD user requirements, the project objective is to create a methodology and develop a decision-support system that will link the site training mission with the planning needs for biological conservation and resource management on DoD installations. The development of IDLAMS supports several DoD user requirements essential to sustaining the long-term military mission, including:

1) Ecosystem approach to land management
2) Land capability characterization
3) Protection of threatened and endangered species, and
4) Erosion control

Specifically, the project addresses several thrusts within the Conservation Pillar of the Tri-Services Reliance R & D Strategic Plan (green book), including Thrust 4A: Natural and Cultural Resource Data Integration and Reporting; Thrust 4B: Range/Training Carrying Capacity;

Thrust 4D: Land Management and Scheduling; Thrust 4I: Range/Training Area Revegetation; and Thrust 4K: Sensitive Ecosystem Management. The IDLAMS methodology will also assist in attaining the goals of the Legacy program. For example, in order to preserve multiple endangered species, cultural resources, biological diversity, and ecological resources, it is necessary to recognize that their preservation may conflict with each other and with site military operations. A complex comprise will usually be required, but there may be hundreds of possible compromise land-use strategies. IDLAMS allows these strategies to be searched and compared to find the best ones. In this way, it is possible to link to the Legacy program with site operations in an effective manner. This project complements other DoD efforts, such as carrying capacity, threatened and endangered species protection, vegetation mapping, ecological modeling, and ITAM initiatives.

The technical approach incorporates various dynamic landscape-modeling components (e.g., training disturbance factors, succession) and integrates them with a GIS and a decision-analysis system (e.g., a value-based tradeoff analysis program, optimization procedures, rule-based expert system). This dynamic, integrated modeling system will be accessed by the natural resources manager via a graphical interface (GUI). The GUI allows the user to input data, make assumptions, and set modeling parameters through a series of prompts while the models and GIS operate in the "background" thereby allowing the planner to implement the program without significant knowledge of computer programming or GIS operations.

The major modeling component is the development of a vegetation dynamics models that classified vegetation physiognomically on the basis of its response to different types of disturbance (both natural and human-induced) and land management actions (e.g., planting). Multiple, spatially distributed disturbances and management activities can be evaluated in terms of their short-term and long-term effects on the landscape. In addition to the vegetation dynamics model and related model components (e.g., fire spread, soil erosion, habitat suitability, hydrology), the approach will use methods that can (1) incorporate guidelines for determining the spatially explicit processes that occur within a study site: (2) use value-based modeling to assess tradeoffs among management objectives (e.g., reduce soil erosion, enhance the training mission, provide suitable wildlife habitat), resource strategies (e.g., planting trees or grasses, temporally or spatially modifying human activities), and cost constraints (e.g., budget allocation, manpower limitation); (3) identifying approaches for coordinating land-based carrying capacity succession models and other relevant tools, models, and systems being developed by USACERL within the overall dynamic landscape modeling components of IDLAMS; and (4) investigate the use of advanced remote sensing technologies to provide large-scale, high resolution images for use in the overall dynamic landscape model. The IDLAMS methodology will be complementary to computer systems and data efforts underway at USACERL.

<u>7.1 Landscape Dynamics and Disturbance Model</u>: The central functional component of the IDLAMS system is a model of vegetation (land-use) change, which incorporates both endogenous changes and those resulting from management activities and disturbance. For the purposes of land management at military bases, it is not necessary to model the fate of every vegetation type, but merely the basic physiognomic classes (forest, grassland, wetland). A basic framework of vegetation types and their transitions will be worked out for IDLAMS that will apply to most military bases and DOE sites. The second type of transition is that resulting from management

actions. For IDLAMS, a list of possible (feasible) management actions and their effects will be compiled, along with their costs. Included in this list will be costs for rehabilitation actions, such as restoration of a severely eroded hill slope or wetland.

7.2 GIS/Model Integration: In IDLAMS, GIS is used far more than mapping alone. First, the interaction between the locations of management actions and their effect on vegetation will be explicitly modeled in the GIS, with the GIS acting as the database to store and update vegetation-type changes on a spatial basis. Second, some components of change will be modeled in the GIS in a spatially explicit manner. For example, at Fort Riley, forest has spread rapidly on newly acquired land, but all new forest adjoins existing forest and most occur in stream valleys. The process of forest spread is being modeled with a spatial contagion model. Other such spatially explicit processes to be modeled include fire spread and training damage. The basis for modeling changes in vegetation is the vital attributes scheme of Noble and Slatyer, which classifies vegetation physiognomically based on its response to different types of disturbance. For example, species respond differently to such disturbances as flooding, fire, trampling, etc. Different vegetation types and successful stages are identified, and a matrix is then developed showing the transition times for natural succession and for responses to disturbance. This matrix identifies the consequences of management actions or disturbances, such as fire, tree planting, fertilization, and tracked vehicle activity, in terms of changes in vegetation type. This approach allows multiple, spatially distributed disturbances and management activities to be evaluated in terms of their short-term and long-term effects on the vegetation and the landscape. It also allows recovery from disturbance to be modeled.

7.3 Value-Based Decision Analyses: In order to evaluate tradeoffs among conflicting objectives in land use, utility functions that quantify the decision makers' preferences are needed. First, utility functions that measure the desirability of different potential land cover configurations for various management purposes (e.g., mechanized training) are needed. USACERL will help define these utility functions. Second, costs are included as a function to be minimized. This helps guide the selection of management scenarios away from those that lead to severe site degradation, with their concomitant high rehabilitation costs. Third, utility functions are needed for Legacy and conservation program values, such as wildlife habitat and biodiversity. Utility functions for wildlife habitat will be developed based on general classes of wildlife and their responses to habitat factors. Other conservation factors such as special habitats and archaeological sites, will be incorporated by giving a weight to the preservation of these fixed map locations during land-use allocation. All these factors must be integrated internally by defining weights for the different fundamental land-use objectives, and externally (with the rest of IDLAMS) by using available land and simulation data as inputs to the utility functions.

7.4 Project Tasks: The major objective of this proposal is to expand, refine, and integrate the current dynamic landscape community model developed for Fort Riley into a more generally useful IDLAMS system for all military installations. The three major tasks to be undertaken are to: (1)model vegetation classes and dynamics, (2) develop utility functions for various landcover configurations, and (3) incorporate appropriate optimization procedures into the IDLAMS system. Additional, project enhanced tasks include: (1) identify approaches for integrating land-based carrying capacity succession models and other relevant tools, models, and systems being

developed by USACERL within the overall dynamic landscape modeling components of IDLAMS; (2) investigate the use of advanced remote sensing technologies to provide large-scale, high resolution images for use in the overall dynamic landscape model; (3) examine additional guidelines and approaches used for evaluating biological diversity; and (4) further improve the optimization programming/trade-off analysis by examining artificial intelligence-based approaches such as the more conventional approaches.

8. Expected Payoff:

The IDLAMS system will reduce costs, enhance land-use management responsiveness and effectiveness, disencumber military operations, enhance environmental compliance, and reduce conflicts between competing land uses. The system should also be usable at DOE and other federal facilities and for resource management on federal lands. In this way, dual-use technology will be developed with broad applicability to federal agencies.

9. Milestones/Accomplishments:

1. Program Start	12/94
2. Visit DOE/DoD Test Sites	04/95
3. Data Acquisition (Determine data gaps)	05/95
4. Preliminary Data Development	07/95
5. Initial Model Development	09/95
6. Remote Sensing Development	08/95
7. Initial Model Development	09/95
8. Optimization/Valuation Development	09/95
9. Graphical User Interface Development	09/95
10. Visit with Ft. McCoy Resource Staff	10/95
11. Ft. McCoy Progress Review	12/95
12. Project Summary and Direction Update	11/95
13. Advanced Remote Sensing Analysis Findings	12/95
14. Summary Ft. McCoy Data and Technical Needs	01/96
15. Framework for Ft. McCoy Vegetation Succession Model	03/96
16. In Progress Review	05/96
17. Identify Additional Resource Models for Ft. McCoy	06/96
18. Final Remote Sensing Products for Ft. Riley	07/96
19. Value-based Tradeoff Analysis Model	08/96
20. Interim Report	11/96

A number of IDLAMS project tasks have been accomplished within the past year of SERDP funding, including:

(1) Expansion, refinement, and integration of the existing Ft. Riley dynamic landscape community model into IDLAMS by modeling vegetation classes and dynamics, developing utility functions for various land cover configurations, and incorporating optimization procedures; includes site visits to both Ft. Riley, Kansas, and Ft. McCoy, Wisconsin;

(2) Identification of approaches of integrating land-based carrying capacity succession models and other relevant tools, and system being developed by USACERL within the overall dynamic landscape modeling components of IDLAMS;

(3) Investigation of the use of advanced remote sensing technologies to provide large-scale, high resolution images to support vegetation assessments for use in the dynamic landscape model;

(4) Examination of additional guidelines and approaches used for evaluating biological diversity to be incorporated into the modeling systems, as appropriate;

(5) Improvement of optimization analysis by examining a number of decision analysis approaches, such as evolutionary algorithms, neural networks, and expert systems, in addition to the more conventional decision analysis approaches. Decision analysis techniques for value modeling were selected for further development. This work included a two-day workshop held at Argonne with ANL, USACERL, and Ft. Riley and Ft. McCoy staff members, followed by the development of a land management strategy evaluation module based on these findings;

(6) Data review and synthesis for Ft. McCoy to evaluate data available for GIS and predictive modeling;

(7) Evaluation of links between computer tools and data input and output flows;

(8) Literature review is being undertaken as a basis for ecosystem, scientific, and technology research and development;

(9) Project efforts have focused on leveraging SERDP program funding and accomplishments, familiarity, and coordination with related DoD and other federal efforts;

(10) Assist in coordinating role with other research laboratories that have conservation program projects that related to the IDLAMS project.

10. Transition Plan:

In order to transfer IDLAMS analytical tools to the military, ANL will arrange technology transfer with USACERL. IDLAMS analytical tools are being designed to be complimentary with USACERL systems.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	Total
SERDP	863	50	750	430	1,793

12. Performers:

Work will be performed by ANL and USACERL. Fort Riley and Fort McCoy will be used as test sites. ANL has extensive experience and expertise in environmental assessment, restoration, conservation, environmental compliance, GIS, and software development. Dr. Sundell leads the Ecology and Natural Resources team for Argonne's Energy Systems Division, Center for Environmental Restoration Systems. He has extensive experience in biogeographic research, land-use planning and natural resources management, spatial analysis, and environmental assessment, including the management of large projects funded by the U.S. Army. Ms. Sydelko, a soils scientist and botanist, administers the Land Resources Analysis Lab for the Energy Systems Division and has done assessment and applied research projects for the military, utilities, and DOE. Ms. Majerus directs research and development projects utilizing spatial, relational, and temporal analysis and GIS technology, relational database management systems, and graphic user-interfaces for integrated natural and cultural resource management and ecological analyses for personnel on Army installations. Her recent accomplishments include development and delivery of the PRISM computer decision support system for Ft. Polk, LA. In addition to the principal investigators listed, the project is supported by a full contingent of environmental and natural resource researchers, decision analysis experts, and computer scientists.

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14. Keywords:

Conservation, Legacy, Wildlife, Habitats, Geographic Information Systems, Ecological Modeling, Decision-Analyses

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Predicting Environmental Impacts Resulting from Winter/Cold Climate Military Training

3. **Agency:** U.S. Army

4. **Laboratory:** Cold Regions Research and Engineering Laboratory (CRREL)

5. **Project ID:** #1047

6. **Problem Statement:**

The direct tie between realistic training and operational readiness can be no more obvious than the impact of the National Training Center (NTC) on our success in Desert Storm. Compared to other environments such as the desert at the NTC, the Army has trained proportionally little for operations in winter and cold climate conditions. The ramifications of this are decreased readiness and capability for the full range of Army missions in areas such as Korea and Bosnia. The lack of emphasis in winter/cold climate (W/CC) training is partially due to the past mission emphasis on desert and tropical climates and partially due to the geographic location of many of the more intensely used training areas. The greater difficulty and potentially higher costs of W/CC training due to equipment, people and environmental management issues have also been contributing factors. As a result, relatively few troop units actually experience significant winter training.

There is a significant gap in overall knowledge and experience for conducting W/CC training. The guidance currently available does not allow land managers and trainers to increase the training opportunities on existing training areas and to reduce the cost of achieving the necessary readiness for W/CC operations. There are significant lessons learned and experience from training activities in Alaska and northern tier facilities such as Ft. McCoy, WI, Ft. Drum, NY, Camp Ripley, MN. as well as Europe and Korea that can serve as a basis for increasing the Army's overall ability to train for winter and cold climates. These experiences, combined with the additional knowledge of the physical environment of cold regions at CRREL, will provide the foundation for significantly increased training opportunities in W/CC and more efficient usage of existing training lands.

7. **Project Description:**

The objective of this study is to develop the basic information, strategies and management tools to increase W/CC training opportunities on existing training lands for a greater level of readiness for W/CC operations. This includes the ability to plan for effective training to the capacity of the training lands, criteria for optimum space-time scheduling of training lands and activities, methods to sustain the training environment to its greatest functional capacity and approaches for

monitoring and management of the environmental resources to facilitate opportunities for real time and frequent optimization of resource utilization.

there are special advantages to increasing training activities in winter. Along with the need for increased readiness for W/CC operations, many lands are more resilient to intense training in winter and cold conditions because of the presence of snow cover, the high strength of frozen ground, the heartiness of cold regions vegetation species while in a dormant state, and the reduced interactions with wildlife. Shifting more of the training load to winter and cold months may serve to dramatically reduce the adverse impacts of training during the growing seasons.

The special aspects of the winter and cold climate environments are the key to this endeavor, both from the types of W/CC training needed and the optimal utilization of training resources in located in cold regions. The current practice for training in Alaska and sites in Europe such as Hohenfels and Grafenwoehr will be coupled with a definition of the training activities that are the most challenging for W/CC conditions to develop a prototype set of activities that must be supported. Additional insights can be derived from the Marine Corps experiences in meeting their Norway mission through winter training at Ft.McCoy, WI and Pickle Meadows, CA.

Prototype planning procedures will be developed to establish a baseline physical status of the training area relevant to W/CC conditions. This will form the basis for projecting the types and levels of activities that can be sustained for any given time period. Practical methods to monitor the status of the areas will be derived form existing R&D on remote and insitu sensors. Models of processes that govern the condition and capacity of the different environments of the W/CC training area will be integrated to form a simple, but quantitative, scheduling and management tool. Existing R&D on revegetation and erosion control practices will be leveraged to develop approaches to sustaining a high degree of training capacity. Finally, general guidelines on practices that optimize W/CC capabilities will be developed. These products will be demonstrated at one facility in Alaska such as Fort Wainwright and another in a norther tier state such as Ft. McCoy, WI, Ft. Drum, NY, or Ft. Riley, KA. These products will take advantage of existing data bases and information management tools and be based toward simple, functional procedures that allow the training professionals to value add their experience and expertise.

8. Expected Payoff:

This work will result in a greatly enhanced ability to train in W/CC conditions, dramatically increasing the Army's readiness in these especially challenging conditions. It will increase the utility and utilization of current training areas and offer reduced unit training costs. It leverages a multitude of ongoing research both within the Cold Regions Research and Engineering Laboratory as well as the Construction Engineering Research Laboratory programs and the academic community.

9. Milestones/Accomplishments:

1. Define training requirements for realistic W/CC training Type, Intensity and Time FY 96

2. Configure prototypical planning and modeling products for user scrutiny FY 96
3. Inventory W/CC training resources (available site, capacities) Conduct workshop with training community FY 96
4. Generate prototype planning and decision making methodology, Architecture, Models, Data integration and availability FY 97
5. Generate monitoring system for environmental parameters/processes conducive to effective training. Ground state assessment (frozen soil, snow cover, freeze/thaw), Vegetation state assessment (dormancy periods, snow protection) FY 97
6. Integrate and Demonstrate Training Resources Management Package Develop and demonstrate monitoring systems. Develop final models of training processes FY 98
7. Guidelines for optimum W/CC training land usage. Workshop with trainers/managers FY 99
8. Interim Report on Correlation of Bench-scale and Test Apparatus Results 10/96

10. Transition Plan:

The transition of this work will be started immediately. The first major activity of the program will be a workshop to capture and incorporate ideas and needs of the user community. Land managers and trainers will be involved in outlining the products, the means by which those products will be applied and the demonstrations of the technologies as they are developed. A pilot study will be initiated during the first year to configure prototypical products for different types of training in different types of W/CC conditions. This effort will allow clear and direct feedback from the land management and training communities early in the program, providing strong early focus for the program by the users. Finally, demonstrations will be conducted on a number of training lands in Alaska and the northern tier of states to verify the developed technical products. The training and land management communities will also be integral to the teams that produce the final guidelines for W/CC training.

11. Funding: $(K)

	FY96	FY97	FY98	FY99	Total
SERDP	500	700	700	400	2,300

12. Performers:

This program will be performed by the Cold Regions Research and Engineering Laboratory (CRREL) with significant support from a number of universities and the Army Directorates of Public Works (DPW) organizations at the military installations selected for demonstration of the products developed. CRREL is the nation's leading R&D organization for cold regions physical and environmental sciences. It brings a global understanding and analytical modeling capability for cold regions processes and military functions that is unparalleled. The diverse talent resident at CRREL, the university partners with which CRREL commonly interacts, and the close rapport of CRREL with DPW personnel at many norther and Alaska bases, provide a distinct opportunity for this program to make extraordinary progress over the expected duration of the study.

13. Principal Investigator:

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14. Keywords:

Training, Winter/Cold Climate

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Initial Framework for Assessing Military Training and Testing Impacts on Natural and Cultural Resources

3. **Agency:** U.S. Army Corps of Engineers

4. **Laboratory:** Construction Engineering Research Laboratories

5. **Project ID:** #1048

6. Problem Statement:

Military training and testing potentially result in impacts on ecosystems and habitats, biodiversity, threatened and endangered species, soil and water quality, archeological sties, and other Department of Defense (DoD) natural and cultural resources. The potential impacts may be (1) physical, chemical, noise, biological/behavioral, (2) direct or indirect, (3) short-term and/or long term, (4) climatological, and (5) cumulative, additive or synergistic.

There are also indications that many types of military land use (in general) may be less destructive, in the long term, to plants and animals and their habitats than other, more familiar, civilian intensive land uses such as agriculture and urban development. This apparent phenomenon must be investigated, and the relative impact of military training and testing land uses must be put into context with other surrounding land uses.

Conversely, the need to ensure long-term sustainability of training and testing areas, and to comply with environmental laws and regulations, which may entail constraints on the military training mission. Modern proactive management of training lands and resources must seek to minimize these constraints while meeting stewardship and legal requirements.

The 1995 Defense Science Board on Environmental Security recommended an integrated and proactive conservation program within a risk management framework. The DoD research community has developed and adapted some data and models relating to specific military impacts. However, DoD lacks an integrated impact assessment framework that would relate multiple training and testing impacts on different kinds of natural/cultural resources, and serve as a basis for planning and execution of both research and management of natural and cultural resources. A risk management approach will require adequate and standardized data and models dealing with military training and testing impacts. A prioritized risk management approach is necessary for DoD due to fiscal and operational constraints which preclude immediate solutions for every risk to natural and cultural resources.

7. Project Description:

Technical Objective: The primary objective of this research is to develop/provide documentation which identifies methodological approaches and procedures and data requirements as well as existing sources of data to quantitatively assess military training and testing impacts on natural and cultural resources in all different types of environments. The product of this effort will be a guide for design of valid, quantitative research and data collection programs to provide assessment results which will be accepted by agencies outside DoD. This product also can serve as the foundation to develop a framework for conducting risk-based assessments of these impacts.

Technical Approach: An Advisory Group of selected DoD, EPA, and DOE research personnel who are experts in natural/cultural resources research and/or impact assessment will be formed to review results of Tasks 3 and 4 and advise on Tasks 5 and 6. The Advisory Group will meet after completion of Tasks 3 and 4. Completion of this project will require documentation of existing information by reviewing literature. DoD documents, and DoD and other government research reports. In addition, selected DoD personnel will be interviewed. Impact assessment data requirements and existing data sources will be identified. The work will be coordinated with and reviewed by selected representatives for the DoD, Air Force, Army, Navy and Marines.

The following specific tasks will be completed to accomplish the objective of this research:

Task 1. Summarize DoD Conservation Objectives. Current policy statements, legislation, and strategic plans will be reviewed, analyzed, and summarized. Selected DoD policy makers will be contacted and interviewed in person and/or by telephone for background information on current policies as well as for perceived future trends.

Task 2. Analyze Military Training and Testing Land, Water and Airspace Use Requirements. Sources used will include current military documents (including training manuals), and personnel in the military training and testing organizations from all service branches. USACERL will analyze the information and compile it into a unified assessment of requirements. USACERL has previously developed some documentation for Army and Air Force requirements. In addition, USACERL is currently coordinating extensively with Army training personnel to verify training land use requirements for land carrying capacity. Similar coordination will be established with the Air Force, Navy and Marines. The U.S. Army Cold Regions Research and Engineering Laboratory (USACRREL) is analyzing requirements under cold weather conditions.

Task 3. Convene Advisory Group. The Advisory Group will convene after completions of Tasks 3 and 4 to review the results of those tasks. The group will also provide advice and review for Tasks 5 and 6.

Task 4. Identify and Describe Types of Impacts Expected from Military Training and Testing Uses. Impacts in all different types of environments, including terrestrial, aquatic, marine and temperate and cold. These impacts will be generally described for this planning effort. Information will be obtained by reviewing selected literature (open literature, DoD reports, other government reports), reviewing ongoing research program documentation (e.g. Army Integrated

Training Area Management (ITAM) research; DoD ODUSD(ES); US EPA Biodiversity Research Consortium), and interviewing researchers conducting current studies. Potential impacts will be identified from information in the literature and from researchers and based on professional experience and expertise. Uses of land, water, and airspace will be related to potential impacts using an easy to follow display technique such as a matrix or flow diagram. Impacts considered will include cumulative, additive or synergistic impacts and ecosystem-level effects, but specific information on these effects is beyond the scope of this initial effort.

Task 5. Identify Data and Procedures Requirements to Assess Military Training and Testing Impacts on Natural and Cultural Resources. Data and procedures required to quantitatively assess effects will be identified based on literature, interviews, and professional expertise. Data needs considered will include exposure, effects, and dose-response for physical, chemical, biological and acoustic impacts; data required to assess subtle (e.g. behavior) and long-term effects; and scales and quantity required. Differences in varying environments, e.g. cold versus temperate addressed. Gaps in knowledge of impacts of military training and testing activities or approaches to assess them will be identified.

Task 6. Identify Existing Data Sources, Databases, and Data Collection Programs. Existing data sources will be identified from literature, reports and other DoD personnel and sources; DoD organizations conducting data coordination/evaluation initiatives (e.g. the Defense Environmental Security Corporate Information Management (DECIM) system, the Air Force-led Environmental Technology Support Center (ETSC), the Army Environmental Policy Institute (AEPI), and the Army Environmental Center (AEC)); and from ongoing research programs within DoD. If time and resources permit, data sources from other government agencies will be identified, e.g. USGS, NCRS, NBS. The data sources will be screened for potential applicability to integrated, risk-based impact assessment and management of military lands.

Technical Issues to Overcome: A paucity of information on ecosystem-level efforts in general and limited information on effects on natural and cultural resources from some military training and testing activities place limitations on the completeness of the descriptions of expected impacts which can be developed in Task 4. Considerable bias against conduct of military training has affected non-quantitative evaluations of defense activities in the past. Quantifiable, reproducible results must be identified where possible to overcome this potential barrier to acceptance of the results in this study. Specific identification and definition of relevant specific data collection methods for identified potential military training and testing impacts on natural and cultural resources is beyond the scope of this effort. Types of data requirements will be addressed.

8. Expected Payoff:

Payoff to the military from the product of this research will be a more cost-effective return for the research funds invested. The work will provide a guide for development of valid, quantitative research and data collection to provide assessments of impacts of military activities on natural and cultural resources which will be accepted by agencies outside DoD, including regulatory agencies. In this context, the work accomplished in this project will provide the foundation for

further development to fully realize the recommendation of the Defense Science Board. The documentation produced will also be a compilation of current knowledge upon which to build an integrated impact assessment framework. This framework would establish a new approach to natural and cultural resources-management on military installations. The new approach is a risk-based strategy for management of military lands. To support the risk-based strategy, information form this study can be used as the basis to develop a framework for risk-based assessment of impacts of military training and testing activities.

Ultimately, by supporting a risk-based approach, the tools provided from this research and a subsequent framework development will assist decision makers within DoD to identify their knowledge gaps and prioritize their research and data collection needs for natural and cultural resources management to address the greatest risks first. This prioritization will help focus research to support the military mission. When the framework is developed, it will also support of risk-based context which will assist DoD to better conduct training and testing activities while complying with environmental regulations, maintaining training and testing realism, and maintaining stewardship of natural and cultural resources. The framework, in turn, would be the starting point for future research to fully develop a risk management approach.

9. Milestones:

1. Complete policy documentation and use requirements	04/96
2. Convene Advisory Group	04/96
3. Complete analysis of impacts and information requirements	07/96
4. Complete identification of data sources	08/96
5. Submit initial plan for workshop to provide recommendations to SERDP for development of framework	08/96
6. Develop transition plan	09/96

10. Transition Plan:

A specific Transition Plan for transfer to DoD personnel will be prepared and coordinated with the SERDP Office as part of this effort. This plan will define/recommend applications of the information developed in this study and identify applications.

11. Funding: $(K)

FY96
100

12. Performers:

The lead agency is the Construction Engineering Research Laboratories. Collaborators include: US Army Cold Regions Research and Engineering Laboratory, US EPA, Argonne National Laboratory. Advisory Group Members/Reviewers: include, L.J. O'Neil from Waterways Experiment Station, C. Racine from CRREL and B. Mandel from the Topographic Engineering Center.

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14. Keywords:

Natural Resources, Cultural Resources, Cold Environment, Impacts, Impact Assessment, Risk Assessment, Military Activities, Military Training, Military Testing, Military Land Management.

SERDP FY96 Project

1. SERDP Thrust Area: Conservation

2. Title: Threatened, Endangered, and Sensitive Resources

3. Agency: U.S. Army

4. Laboratory: Construction Engineering Research Laboratory

5. Project ID: #507

6. Problem Statement:

Nearly 1,000 species in the US are protected under the Endangered Species Act (ESA), while thousands more are candidates for listing. Over 300 listed and candidate species, in addition to nearly 300 state listed species and species of concern, are known or suspected to reside on Army lands. This results in : (1) mission constraints and impediments to land acquisition, potentially leading to reduced defense readiness; (2) lengthy and costly litigation; and (3) criminal and civil penalties. As the number of listed species increases, mission constraints and management burden also increase. Our ability to address this issue is limited because of inadequate information on distribution and abundance of TES and their habitats on military land, the effects of mission activities on TES and supporting ecosystems, and appropriate mitigation and management options.

The major objectives of the TES research program are to provide DoD land managers with: (1) tools and capabilities to inventory and monitor TES, and to evaluate impacts of military operations on TES and their habitats in an efficient, effective, and scientifically defensible manner, (2) practical approached to mitigation of Army-unique impacts, and (3) predictive capabilities to evaluate effects of proposed use on TES populations, habitats, and the ecosystems upon which they depend.

7. Project Description:

Our goal is to establish the Army and participating services as national leaders in proactive conservation of threatened and endangered species (TES) and the ecosystems upon which they depend as an integral part of our mission. Our intent is to establish a coordinated, programmatic approach to TES- related research and technology transfer on military lands, and to provide capabilities to avoid mission impacts while enhancing efforts to meet national, DoD, and Army TES-related conservation goals cost-effectively.

Technical Objective: Specific technical objectives are to: (1) develop regional guidelines for TES habitat evaluation and management; (2) evaluate approaches, methodologies, and techniques to enhance conservation of TES plant population; (3) develop technologies to assess impacts of smokes, obscurants, and CS agents on TES; and (4) initiate development of a regional endangered species interagency workshop. Our intent is to integrate these specific research activities in a broader programmatic approach to TES research.

Technical Approach:

Regional Habitat Evaluation and Management Guidelines: Regional TES management guidelines will be developed for one region using a plant community framework. Regions will be designated according to geographic location, major plant community types present, and potential for supporting populations of the same species complexes. A prototype management plan will be developed for one region. The specific TES evaluation protocols and management strategies developed will apply to several installations within the region. Plant community association and species habitat requirements will be defined based on existing literature, coordination with species and community experts from other universities and private organizations, and expertise of installation land managers. Management strategies will be developed that apply for a given plant community type across the region.

Enhancing Survival and Recovery of TES Plants: TES plant population enhancement approaches will be evaluated for use by installation managers. The capability to enhance TES plants in areas least likely to conflict with the military mission is desirable as one viable mean to mitigate Army-unique impacts on these species. The approach, methodologies, and techniques researched are intended to assist installation managers to effectively enhance species population and habitats so as to avoid mission conflicts. The plan is to use a team approach to scope the issue, evaluate potential enhancement techniques, and demonstrate specific enhancement guidelines. A scoping workshop will be conducted to address the legal and ethical considerations, the selection of potential areas/installations and species of interest, and ways of determining success. Small-scale field studies initiated earlier will be continued.

Impact of Smokes, Obscurants & CS Agents: A thorough evaluation of existing documentation on the use of S-O&CS, the known and probable impacts of these materials on plants and animals, including an evaluation of materials currently in development to the extent possible; and research protocols currently applied will be completed. Smoke toxicity will be determined based on existing documentation. We will identify species most likely in jeopardy due to exposure to these materials, and mission activities most likely constrained significantly as a result of species sensitivities. A conceptual approach to development of models for the impacts of S-O&CS on TES will be developed. Field research protocols developed earlier will serve as the basis for small scale, preliminary field study design evaluation.

TES Regional Workshop: We will initiate planning for a regional TES interagency workshop to take place in the southeastern US. A workplan will be developed, an agenda developed in coordination with the US Fish and Wildlife Service and the National Biological Service, and an announcement sent out.

Relationship to DoD/DOE Environmental Objectives: The proposed work supports many of the Department's goals and objectives as specified in SERDP guidance documents. Specifically, our intent is to: (1) provide capabilities to unencumber military operations while protecting sensitive resources cost-effectively, (2) contribute leadership in addressing a pressing national environmental problem, (3) facilitate information exchange among governmental and nongovernmental agencies and the private sector, (4) avoid duplication of effort among these groups, (5) investigate potential applications of technologies developed for national defense purposes, and (6) encourage joint interagency R&D and demonstration projects.

Relationship to Similar On-Going Work: On-going research under the Army's Long Range Science and Technology Program (LRS&T) includes: "Inventory and Monitoring Standards for TES on Army Lands", "Military Noise Impacts on Rare and Endangered Species", "Threshold Impacts for Maneuver Disturbance", and "Threshold Impacts for Smoke and Obscurants". We are also working cooperatively with Oak Ridge and Argonne National Laboratories on " Ecological Modeling for Military Land Use Decision Support" and "Strategic Natural Resources Management Methodologies" respectively.

Tri-Service Environmental R&D Strategic Plan: This work is intricately related to DoD Pillar #4, Conservation. The specific thrust directly addressed is 4.F: "Threatened and Endangered Species". Specific user requirements supported include: (1)Impacts of military operations on TES, (2) Mitigation of Army-unique impacts, and (3) Habitat suitability predictive modeling.

8. Expected Payoff:

These efforts will contribute one piece to a comprehensive, systematic, and integrated approach to TES management on military lands. Resulting products will support the Army's environmental and endangered species management strategies, and aid in efficiently meeting Army TES policies and regulatory requirements. Through this effort, the military will develop and demonstrate scientific and technical leadership in the management of TES. We will thus be better able to integrate TES considerations with military activities while avoiding mission impacts. Expected return on investment is high. On-going interagency coordination will yield benefits at national, regional and local levels. Potential users include Army and other military elements at installations, MACOM, and DA levels who are responsible for TES management. Products will also transition to interagency and private sector partners.

9. Milestones/Accomplishments:

Regional Habitat Strategies

1.	Define geographic regions	03/94
2.	Select species and habitats for evaluation	06/94
3.	Conduct background survey on 1st set of species	09/94
4.	Complete draft concept plan and status report	09/94
5.	Complete TR on concept plan and status report	08/95

6.	Assess habitat requirements and complete draft species profiles for selected species	08/95
7.	Assess potential impacts of military operations	09/95
8.	Complete drafts of selected plants community abstracts	09/95
9.	Identify existing habitat/community assessment strategies for TES management	08/96
10.	Complete additional plant community abstracts and species profiles	09/96
11.	Develop habitat management strategies for selected species	04/97
12.	Complete prototype regional handbook	

Enhancing Survival and Recovery of TES Plants

1.	Literature review and evaluation report on current methods	09/94
2.	Scoping workshop	12/94
3.	Report on scoping workshop and research plan	02/95
4.	Preliminary guidance for installations	10/95
5.	Comparative evaluation report of various techniques	09/95
6.	Progress report on Ft. Stewart plant work	06/96
7.	Guidelines for TES plant enhancement	
8.	Complete field studies	03/97
9.	Final report on field studies	09/97

Smokes, Obscurants & CS

1.	Complete evaluation of existing documentation on impacts of S-O&CS on TES	09/94
2.	Develop list if species most likely to be impacted by S-O&CS	09/94
3.	Conceptual model addressing impact of selected S-O&CS on a species	03/95
4.	Select species and sites for filed studies	05/95
5.	Initiate small-scale field evaluations in preliminary field trials	09/95
6.	Complete preliminary risk assessment for effects of fog oil on Red-cockaded Woodpecker	12/95
7.	Determine smoke toxicity levels for selected species	03/96
8.	Complete field work	05/97
9.	Complete risk assessment for effects of fog oil on Red-cockaded Woodpecker	08/97
10.	Report results of field work; recommendation for follow-on studies	09/97

TES Regional Workshop

1.	Develop workplan for a regional interagency TES workshop (southeast and southwest)	06/95
2.	Develop/finalize agenda in coordination with NBS and USFWS (CERL and WES coordination)	07/95
3.	Prepare and distribute workshop announcement	08/95

In coordination with the TES User Working Group, we have established Fort Stewart, GA as our model installation for further development and application of TES-related research products. This allows us to leverage limited resources toward resolution of pressing TES problems, the products of which can be transferred to other installation within the region. Work with other installation in the region is being pursued as the need arises.

Regional Strategies: Completed final draft of the concept plan and submitted it for editorial review. Finished 10 Faunal Species Accounts and two Plant Community Abstracts. A draft report entitled, "Potential Military Impacts to Selected Plant Communities in the Southeastern US" was also completed. A poster was presented and well received at the Annual Meeting of the Wildlife Society, and a paper presented at the Annual DoD Forestry Workshop,

Enhancing Survival and Recovery of TES Plants: Field work at Ft. Stewart uncovered 14 new population of Balduina atropurpurea. Only six populations were previously known on the installation. Range-wide, only 11 of 39 populations had been verified in Georgia in the last 15 years. Fort Stewart has the highest quality populations of the species so there is a good possibility that these populations will contribute significantly to the species survival.

Smokes and Obscurants: A smokes dispersion model was implemented in GRASS GIS for use in evaluating impacts of fog oil smokes on TES. A risk assessment for the effects of fog oil smokes on the Red-cockaded Woodpecker is in draft. A report has been complete evaluating options and statistical considerations for evaluating impact of S-O&CS on TES. Field work was begun at Fort McClellan to evaluate smoke detection. methodologies and sampling techniques.

TES Regional Workshop: The Southeastern Interagency Endangered Species Research and Development Workshop scheduled for late November and then mid-January has been postponed due to the federal budget impasse. It was to have been attended by representatives from a variety of federal agencies. We expect it to take place in spring or early summer.

10. Transition Plan:

Technology transfer is an essential element of the proposed work. We are committed to developing useful technology from research projects while reaching out to a broad range of potential users. This includes relevant technologies developed by other TES programs, and distribution of transfer products to government, nongovernment, and private sector entities. Coordination will occur via a high degree of interaction with the user community through user group workshops, periodic newsletters and information bulletins, and establishment of a model installation for product development and implementation.

Several federal agencies presently conduct TES-related research; much of it applicable across agency lines. Mechanisms will be established to share information, and to coordinate TES R&D with appropriate government and nongovernment agencies and other public and private sector organizations. We will avoid duplication of effort, identify opportunities to leverage limited resources to meet common goals, and maximize transfer and use of the best and most advanced technological capabilities available.

11. Funding: $(K)

FY94	FY95	FY96	FY97	TOTAL
805	300	850	210	1,765

12. Performers

The work will be preformed primarily by USACERL with assistance form other USACE Labs as necessary. The Regional Strategies component of this work is being performed in cooperation with USAWES. Leveraging opportunities will be also sought with government and nongovernment agencies and the private sector via interagency cooperation efforts.

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14. Keywords:

Threatened and Endangered Species, Regional Strategies, Habitat Management, Enhancement, Military Impacts, Smokes and Obscurants, CS Agents

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Integration of Radiotelemetry, Remote Sensing and GIS Technologies for Habitat Use and Delineation in Support of Risk Assessment and Restoration Activities.

3. **Agency:** U.S. Department of Energy

4. **Laboratory:** Savannah River Technology Center (SRTC)

5. **Project ID:** #363

6. **Problem Statement:**

The goal of the proposed program is to integrate existing automated radiotelemetry technology with Global Positioning System (GPS), Geographic Information System (GIS)/Heuristic Optimized Processing Systems (HOPS), and land cover information in a way that will increase efficiency, accuracy, and availability of habitat and land cover use data necessary for a variety of ecological activities including:

- waste site characterization
- ecological risk assessment
- performance and success of ecosystem restorations
- habitat use of animal species of concern, such as those listed as threatened or endangered

Historically, habitat use and preference has been very difficult to quantify for many types of organisms. For larger animals, these data are generally collected using radiotelemetry, a method where small radio transmitters are attached to the organisms to be studied. The animals are then located using hand-held antennas connected to portable receivers. Locations of the animals are then surveyed or approximated on a map, or the habitat and cover type are simply recorded. This method requires extensive field time and provides very limited data return for time invested. Organisms available for study are also limited to those large enough to carry radio transmitters. Data for small animals can only be collected through extensive field observation. Current technology in miniaturization is lending itself to much smaller radio transmitters, allowing them to be attached to smaller organisms (i.e. bats, small rodents, snakes, and frogs). There is, however still, the problem of data density, or the amount of information obtained per unit of effort. Automated telemetry systems coupled with existing information technologies could greatly enhance the usefulness of radiotelemetry for habitat use data collection.

7. Project Description:

Technical Objective:

- Refine the existing automated telemetry system with hardware and software upgrades
- Develop software to use data from the automated telemetry system to calculate locations from triangulation
- Interface triangulation locations with GIS layers of habitat types developed from other remote sensing techniques like GPS and over flight data.
- Field test of upgraded equipment within a potential risk assessment area at SRS
- Off-site (non-SRS) demonstration of capability

Technical Approach: The principle technical approach is to integrate existing hardware previously developed by SRTC with other available remote sensing (GPS) and information management systems (HOPS). This will be accomplished through further development of the existing hardware and its control software and development of interfaces to other technologies. Full scale field research will provide testing and verification of the technical approach.

Tasks:

- Upgrade of existing hardware
- Field test of data acquisition portion of project
- Development of triangulation/data analysis software
- Development of HOPS/GIS interface
- Test of integration algorithms and data analysis
- Off-site (non-SRS) demonstration of capability
- Publication of results

Relationship to DoD/DOE environmental objectives: This program supports the mission and objective of DoD/DOE to be leaders among government agencies in applying modern technology to ecological risk assessment, restoration, remediation, and the preservation and enhancement of biological diversity. Specifically, this program endeavors to apply new approaches to old problems of determining specific habitat preferences and use by animals within limited areas. By better elucidating how organisms interact with their habitat on a small scale, ecologists will be much better able to determine what risks a waste site may pose to the surrounding ecosystem.

Relationship to other similar ongoing work: Three areas of other work are directly related to the proposed project:

The proposed project is a considerable expansion of a program initiated during research supporting proposed actions for continued operation of L and P Reactors at SRS. Lotek Engineering, Inc. was commissioned to design and build an automated radiotelemetry tracking system centered around their very advanced SRX400 receiver. The decision to not restart L or P Reactor obviated the need for the system. Upgrading the existing system and integrating it with other remote sensing and information management technologies will allow more accurate and

scientifically defensible characterization and evaluation of waste sites for ecological risk assessment.

The Heuristic Optimized Processing System (HOPS) is a current Office of Technology Development (OTD, project identifier SR1-4-10-17) program at SRS. It is a server-client information system software managing all types of digital information. It will implement hierarchial, network and relational models concurrently or alone to hundreds of end-users. Features include an object-oriented HOPS Toolbox, a Dynamic Index Structure, single-disk-access, record lock out, point-in-time-commit-rollback, fault tolerance defaults, georegistered data sets and photographs, CD-ROM interfacing and a completely open architecture. The goal of the first year's development effort is to provide a system that offers:

- Data basing without cryptic query languages
- Frequently used parameters and nonparametric statistics
- Easy-to-use translators for different data bases and GIS files, spatial analyses of georegistered data
- Immediate access to EPA regulatory support documentation and contaminant databases, and
- Instant switching to other desktop applications used to write risk assessment reports

Advanced Biotelemetry for Resource Management (SERDP project identifier 510, Army, Dr. Seegar, Principle Investigator) shares objectives of field methodologies and natural resource research and management with the proposed project. Technical approaches differ as to scale and method of data acquisition but correspondence between principle investigators has been established and any possible cross development will be pursued.

8. Expected Payoff:

Benefits accrued from the development of automated radiotelemetry and its interface with other remote sensing technologies and GIS could be enormous. The development of very powerful desk top computer data management systems (HOPS for example) will simplify sophisticated analysis of habitat use data. Data collected and analyzed with the proposed system is useful and necessary for many compliance related activities like Natural Resource Damage Assessment (NRDA) activities, characterization of waste sites prior to ecological risk assessment, actual effects and vectors in indicator organisms chosen for ecological risk assessment, and recovery of populations and habitat use within restored ecosystems. The capability of the proposed radiotelemetry system will supply data density on habitat use in order of magnitude greater than that possible with current systems. This will reduce the costs of acquiring necessary information and will provide the benefit of allowing collection of data that is not currently possible to accumulate. Parameters like patterns of habitat use, home range, and behavioral use of space are currently difficult to determine but are important considerations in the evaluation of ecological risk. The ability to precisely evaluate these parameters will greatly improve the accuracy of ecological risk assessment activities.

9. Milestones/Accomplishments:

1. Program start	10/95
2. Begin development of HOPS/GIS data handling software	11/95
3. Field test of upgraded telemetry system	01/96
4. Complete remote power supply for telemetry system	02/96
5. Develop and delineate habitat contour for field test	03/96
6. Full scale field test of telemetry system	04/96
7. Video summary and progress report	05/96
8. Finish first prototype of HOPS/GIS software	06/96
9. Analyze data from full scale field test	06/96
10. Long term demonstration of telemetry system	09/96
11. Analyze data from long-term field test	10/96
12. Interim Report	11/96
13. Complete software development	04/97
14. Telemetry and GPS upgrades as required	05/97
15. Demonstrate equipment at non-SRS location	07/97
16. Begin publishing results of development and use	09/97

10. Transition Plan:

Capabilities of the system will be documented and publicized through publication of the results of the field test of the upgraded system and the analysis of the data collected. Transition of the telemetry system itself will be handled by Lotek Engineering, Inc. through their established private sector marketing network. Transition of the data analysis and GIS interface software will be accomplished cooperatively by the contributors to the program with the assistance of the Technology Transfer organization within WSRC.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	50	100	200	350
DOE/WSRC	25	25	25		75
TOTAL	25	75	125	200	425

Previous funding: Expenditure by SRTC/ESS for development of the original automated equipment, approximately $125,000.

12. Performers:

Currently the only performers involved in the project are SRTC. Lotek Engineering, Inc. has been involved in the project as the developer and vendor of radiotelemetry equipment.Cooperation with A.J. Bowers, principle investigator for the OTD HOPS program will assure timely integration

with that program. Possible cooperation with Wm. Seegar at Edgewood Research, Development, and Engineering Center is probable.

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14. Keywords:

Radiotelemetry, Remote Sensing, Ecological Risk Assessment, Habitat Use, Geographic Information Systems, Global Positioning System

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Whale Monitoring Using IUSS

3. **Agency:** U.S. Navy

4. **Laboratory:** Space and Naval Warfare Systems Command

5. **Project ID:** #48

6. **Problem Statement:**

The Integrated Undersea Surveillance Systems (IUSS) is an oceanic-scale acoustic surveillance system originally constructed to monitor movements of Soviet submarines. Its existence no longer secret, the IUSS provides a unique resource to monitor the populations and movements of several endangered species of marine mammals--specifically, the great whales. In no other way can these movements be monitored over the scale of an ocean basin. Exploitation of this resource is vital in complying with the National Environmental Policy Act (NEPA), the Endangered Species Act (ESA) and the Marine Mammal Protection Act (MMPS).

Present utilization of the IUSS to detect and classify marine mammals is a personnel-intensive effort. Downsizing of the system has reduced the operational personnel currently monitoring IUSS fixed arrays on a 24-hour basis. One important component of this effort will be to automate the detection and classification processes using neural network signal processing techniques.

7. **Project Description:**

The goal of this effort is to continue to apply capabilities of the U.S. Navy Integrated Undersea Surveillance System (IUSS) to monitor various species of marine mammals to contribute towards conservation and regulations compliance. This work explicitly supports the SERDP Goal to "help solve significant...environmental problems through the application of (DoD's) technical capabilities...", several SERDP objectives, all four SERDP Strategy Statements, and Conservation Pillar R&D Objectives 1,3, and 5.

This project will build on the substantial success of the past year and will further enhance the methodologies to exploit the IUSS in support of a variety of national objectives. The Navy demonstration project "SHALES 93" paved the way for the first objective, quantitative analysis of whale populations and migratory movements. Other agencies, particularly NOAA, became convinced of the need to further the results of that effort in order to refine these capabilities into operational tools.

The first of the cooperative experiments with NOAA were conducted in the fall of 1995. "WHALES '95" employed an acoustic array deployed behind a research vessel (R/V), while NOAA-approved observers maintained a visual watch. This was the first attempted intercomparison between visual and acoustic observations of whales. "Northeast Pacific '95" was a NOAA-led effort to determine signal characteristics of great whales at a number of different spatial scales, ranging from near-vessel sonobuoy records to distant SOSUS stations.

This project will concentrate on three main fronts in FY96: (1) a new major experimental effort on whales in the Pacific Ocean; (2) enhancing the interface between the IUSS and potential users; and (3) terminating previous efforts in surveillance aimed at fisheries enforcement.

8. Expected Payoff:

The benefits of this project come in three areas. The first is that through the techniques developed in this work, Navy will be able to be in compliance with major environmental legislation (NEPA, ESA, MMPA) in its test and evaluation of important new systems, including low-frequency active sonar systems. Second, by understanding the movements of the great whales, Navy may minimize its impact on these populations for the entire range of its operations. (The development of automated methods for whale tracking will be of value to NOAA and other agencies tasked with protection and management of endangered species.) Third, this project will enable the opening up of an ocean-wide network of sensors that is otherwise unattainable by the research community. A primary deliverable of this effort is a user-friendly "portal" to Navy's undersea surveillance system. In a time where "big science" costs are being closely scrutinized, it is particularly attractive to consider access to a system which is already paid for.

9. Milestones/Accomplishments:

1.	Final Report NMFS SW Fisheries FY93 Survey	02/94
2.	Navy Ship Shock trials off Southern California	04/94
3.	SURVEYOR ground-truth experiment, NE Pacific	07/94
4.	Completed PODS 93 Test Report	07/94
5.	Final Report, WHALES 93	09/94
6.	Final Report, NE Pacific Driftnet Experiment	09/94
7.	Monitor humpback whale activity off Hawaii	03/95
8.	Neural net simulation testing	07/95
9.	First NE Pacific groundtruth tests	09/95
10.	Support ATOC California Project playbacks	04/96
11.	Groundtruth test joint with NOAA cruise	07/96
12.	Final Report, population estimation using automated long-term statistical monitoring	10/96
13.	Final Pacific Whale Test	10/97
14.	Final Report, IUSS marine mammal pop. estimation	10/97
15.	Establish near-real-time comm. link for data dist.	08/98

In mid-summer 1994, the Navy ran a large test involving an active acoustic transmitter (MAGELLAN II Test). An essential contribution to the test was made by this SERDP program. Personnel from Cornell University participated in this test, using their "POPEYE" software developed during the WHALES '93 Experiment. POPEYE enables a trained user to detect and localize nearby whales data from multiple acoustic arrays. In MAGELLAN II, use if the POPEYE software enabled test personnel to detect the presence of great whales, and alerted the test director to cease or postpone the acoustic transmissions when the whales approached too close to the transmitter.

A preliminary experiment was mounted in the NE Pacific in cooperation with the National Oceanic and Atmospheric Administration vessel Surveyor, in which sonobuoys were deployed from the ship in an area of whale activity. In combining these data with on-board observers and SOSUS data, the definition of experimental objectives for the first intensive experiment effort will be more clearly defined.

Extensive discussions with the National Oceanic and Atmospheric Administration have resulted in the development of a tightly coordinated plan for field experimentation.

10. Transition Plan:

Methods for monitoring whales have been rapidly incorporated into mitigation plans of Environmental Assessments developed by Navy for a series of oceanic tests. (Indeed, these methods have been absolutely essential to the success of such mitigation efforts.) Work is currently underway to institutionalize these methods in Navy mitigation efforts for the whole range of Navy missions and operations.

A close working relationship has been established with NOAA, which has primary national responsibility for monitoring the great whales. A Memorandum of Agreement has been signed by NOAA and Navy on cooperation on environmental issues.

Previous work in the area of fisheries enforcement monitoring will be concluded in the form of a final report which details the methods and needs for employing these techniques to enforce high-seas fisheries treaties.

11. Funding: $(K)

	FY 94	FY 95	FY 96	FY 97	FY 98	TOTAL
SERDP	3,000	1,625	2,400	2,140	800	9,965

12. Performers:

A. Experimental efforts: Cornell University; NOAA Marine Mammal Laboratory; NOAA Pacific Marine Environmental Laboratory; Commander, Undersea Surveillance; Woods Hole Oceanographic Institution; Lawrence Livermore National Laboratory.

B. Interface task: Naval Research and Development Center (NRaD); Applied Physics Laboratory, University of Washington; NOAA Pacific Marine Environmental Laboratory.

C. Fisheries Enforcement task wrap-up: Stanford Research International; ENSCO, Inc.

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14. Keywords:

IUSS, Acoustics, Whales, Neural Networks, Migration, Fisheries

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** The Effects of Aircraft Overflights on Birds of Prey

3. **Agency:** U.S. Air Force

4. **Laboratory:** Armstrong Laboratory (AL)

5. **Project ID:** #89

6. **Problem Statement:**

The Air Force is required to assess the impact of proposed aircraft operations on the environment. Many of the assessments accomplished to date contain unsubstantiated remarks concerning the effects of aircraft noise on wildlife. Prior to 1989, noise studies on wildlife were not well controlled or planned. In 1989 the Air Force began performing several 3-4 year studies on the effects of aircraft noise on wildlife species. These studies are beginning to prove useful for environmental planners at the major command and Air Staff levels to defend the Air Force's requirement to maintain low altitude Military Training Routes (MTR).

Due to issues raised during public scoping meetings and documented concerns with the US Fish and Wildlife Service (USFWS) and the National Park Service (NPS), there is concern that aircraft overflights may disturb nesting raptors (birds of prey). The Air Force embarked on a project in 1989 to review the current literature regarding the effects and, if feasible, to develop an interim model to predict the effects. The interim model was documented in 1990. Since the model is purely hypothetical, it must be validated with empirical data.

7. **Project Description:**

The goal of this project is to verify predictions of a previous 6.3A effort regarding the effects of aircraft noise on birds of prey or raptors (hawks, eagles, falcons, etc.) and to fill in the scientific and technological gaps in the interim model.

The technical objective of this project is to develop a validated dose-response model on the effects of aircraft overflights on birds of prey. The technical approach to accomplish the objective will be to perform field studies on species of interest in an attempt to validate the current model.

Several tasks will accomplish this objective. Task 1, a study protocol, was developed in cooperation with the USFWS to perform field studies to detect differences of 5-30% for productivity rates in spite of large variances in nest success. The study design takes into account such factors as habituation rates, prey abundance and changes in parental behavior that could

affect productivity. This first task examined possible study locations and made recommendation for the best sites near an Air Force installation to perform such a study.

Task 2 is designed to make observations of aircraft overflights in the vicinity of nesting raptors. This task should be performed over a one year period as a minimum to determine the effects of noise on productivity and reduce the impacts of seasonal variations. This task is currently scheduled to be performed over a three year period. It is necessary to coordinate aircraft overflights with the nearest operating command to the study site. Since several previous studies similar to this proposal have been accomplished, these procedures are well known.

Task 3 will attempt to address the effects of aircraft overflight noise on threatened or endangered raptor species, such as Peregrine Falcons and Bald Eagles. This task will form a subset of data obtained from Task 2, were nonthreatened and nonendangered species would be studies.

Task 4 will involve making changes to the current dose-response model and inserting the improved model into the latest version of the Assessment System for Aircraft Noise (ASAN). ASAN is a software tool to assist environmental planners assess the impact of aircraft operations on the environment.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 4: Conservation: Requirement Thrust 4.K., Sensitive Ecosystem Management and 4.P: Training/Testing Impact Studies on T/E.

8. Expected Payoff:

The Air Force will benefit by having a validated model to assess the impact of aircraft noise on raptors. This will greatly assist environmental planners in developing timely EIAP documents and providing answers to questions raised by the general public, SUFWS and NPS. Currently, the USFWS can and has stopped proposed actions with formal Section 7 consultations in accordance with the Endangered Species Act. The goal of this project would be to reduce the concerns raised during these formal consultations and speed up the EIAP.

9. Milestones/Accomplishments: * Milestones will repeat for each field season

1.	Literature review/dose-response model exam	07/94
2.	Research protocol and recommended study sites	07/94
3.	Pilot flight test on Tanana River	07/94
4.	Recruit Graduate student (Tasks 2 & 3)	09/94
5.	Progress report	10/94
6.	Deliver 2 ANM prototypes for testing	12/94
7.	Obtain all field equipment	* 05/95
8.	Identify all nest sites to be observed/monitored for productivity	* 06/95
9.	Complete test flights	* 08/95
10.	Complete observations/monitoring of experimental and control test sites	* 08/95

11.	Determine interim fledgling and productivity rates	* 09/95
12.	Progress report	* 12/95
13.	Evaluate/update field data collection methods	* 12/95
14.	Mount ANMs on animal collars	02/96
15.	Calibrate ANM accelerometers	02/96

In July 1994, the Air Force completed a successful pilot test for studying overflights on the Tanana River near Fairbanks, Alaska. This effort helped direct parameters for the multi-year test protocol, establishing the types of data which could reliably be collected. With the assistance of the USFWS, the first full summer field season was a success. Approximately forty Animal Noise Monitors (ANMs) were deployed at experimental and control sites in the Alaska Yukon MAO training range to gather quantitative noise data on the overflights. Routine behavioral observations were made at both experimental and control sites, including behavioral reactions of the birds to jet aircraft overflights at the experimental sites.

Though the data collected from the first summer field season has not yet been thoroughly analyzed, preliminary review seems to indicate there may be only a small, if any, reaction from the raptors to jet aircraft overflights. These results should be tempered over the course of the multi-year study to reduce the impacts of seasonal variations. The data collected will be used to validate, or update, the current dose-response model and help alleviate concerns raised by the public, USFWS and NPS about the Air Force's requirement to maintain low attitude MTRs.

10. Transition Plan:

The dose-response model resulting from this effort would replace the current interim model in the latest version of ASAN. ASAN was transitioned in FY 95. Since ASAN will accept various effects modules, there will be no risk in changing these two models.

The Air Force will publish a technical report releasable for public distribution through the National Technical Information Services and the Defense Technical Information Center. Papers on this project will also be presented at various scientific meetings.

11. Funding: $(K)

	FY 93	FY 94	FY 95	FY 96	FY 97	TOTAL
SERDP	80	311	80	350	330	1,151

12. Performers:

The Air Force Armstrong Laboratory will be the principal agency performing this work with support from the Air Force: AL/OEBN, 11th AF/LGV. Additional, the Alaska Cooperative Fish and Wildlife Research Unit and the University of Alaska, along with Biological Research, Inc., will also participate in this research.

13. Principal Investigator:

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14. Keywords:

Raptors, Birds of Prey, Aircraft Noise, Disturbance

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Genetic Diversity Monitoring in Plants and Wildlife

3. **Agency:** U.S. Environmental Protection Agency

4. **Laboratory:** Environmental Monitoring Systems Laboratory, Cincinnati, Ohio

5. **Project ID:** #246

6. **Problem Statement:**

Undisturbed natural populations tend to maintain a high degree of biological diversity or polymorphism, but any environmental stress that eliminates a large fraction of individuals from the breeding population can eliminate (by pure chance) important genetic variants. This phenomenon, known as a genetic "bottleneck", leads to a reduction of heterozygosity in succeeding generations. The overall effect is populations with greater vulnerability to future stresses. Therefore, quantitative measures of genetic diversity can be useful as indicators of past environmental insult, as well as criteria for targeting potentially sensitive, i.e., genetically homogeneous populations.

Measurement of population genetic diversity directly supports the SERDP Conservation thrust area as an assessment tool to identify vulnerable populations and subpopulations of many species of animals and plants, and to monitor their responses to ongoing conservation and protection efforts. This project has both basic research and applied research components. Enhancement of fingerprinting technologies and statistical evaluations will continue, especially as new species are examined. Once the analytical strategy for a species or genus is established, it will be applied to a myriad of situations confronting member populations.

7. **Project Description:**

Goal: The goal of this project is to monitor the genetic diversity of feral populations in ecologically sensitive areas using DNA fingerprinting technologies. Loss of diversity resulting from multiple stressors, such as habitat destruction and fragmentation as well as pollution exposures, is a major concern in the conservation of populations of native plants and wildlife. The genetic diversity or total gene ensemble of a population reflects its intrinsic robustness. Loss of genetic diversity leaves a species less able to adapt to new environmental stressors; therefore, loss of population genetic diversity can foreshadow species loss, with resultant loss of biological diversity within an ecosystem.

Technical Objectives: DNA fingerprinting is an accepted technique in medical and forensic sciences for the determination of identity and relatedness of individuals (particularly but not exclusively, humans), and is also attracting attention as a tool for population geneticists to

determine variation at the genetic level within and between populations, both human and nonhuman. Genetic differences between individuals can be demonstrated in species that are otherwise genetically uncharacterized. The summation of DNA fingerprint differences of many individuals provides a measure of genetic diversity in the population from which those individuals are derived.

Technical Approach: In this laboratory, we have developed two different, but complementary, fingerprinting techniques to assess polymorphisms in several species of aquatic and terrestrial animals and plants. The first method relies on the presence of short, repetitive DNA sequences, called VNTRs (variable number of tandem repeats), which exhibit high variability within a population; DNA bands are visualized on a Southern blot of target genomic DNA, using radiolabeled probes specific to the repeat sequence. The second fingerprint method is based on thermal cycle polymerase chain reaction (PCR); DNA marker bands are biochemically multiplied by a cyclical enzymatic reaction with target DNA (this is called the RAPD, i.e., Random Amplified Polymorphic DNS, method). With both methods, genetic polymorphisms are revealed as DNA bands that are generated by the genome of one individual, but are absent from the second individual. By statistically analyzing the distributions of polymorphic bands within populations, indices of population heterozygosity and genetic diversity can be derived for populations of virtually any species.

These methods were initially applied to a set sample of DNAs purified from more than seventy individual brown bullhead catfish representing three populations from both environmentally impacted and clean areas. Preliminary data support our hypothesis that brown bullhead catfish from the most stressed (in this case polluted) aquatic environment are more genetically homogeneous than those from the least stressed environments. Additionally, these methods are now being applied to additional species of wildlife as well as plants, both terrestrial and aquatic.

Also, we have developed an ecologically based method of tissue/DNA acquisition for direct use in RAPD reactions. This simple and rapid technique, which is nondestructive to the organisms samples, obviates the need for radionuclides and isolation, purification and quantitation of genomic DNA for thermocycle amplification reactions. This method combines the powerful tools of genetic analysis with an ecologically favorable means of sample acquisition. This strategy is particularly useful when collecting field specimens for population analysis on endangered species.

Using the raw fingerprint data from both of these methods, several mathematical treatments for assessing DNA fingerprint diversity are being examined and compared in order to determine the best statistically valid approach. This part of the effort was done in conjunction with Dr. Vicki Hertzberg with a Cooperative Agreement funded by SERDP. This Cooperative Agreement ended October 1, 1995, and statistical work is being continued in house by Tony Leonard, a fellow supported by Interagency Agreement with the Oak Ridge Institute. He is currently developing a Bayslan approach to estimating population heterozygosities given the limitations of maximum likelihood estimation when sampled allele frequencies lie on or near the boundaries of the permissible parameter space.

Since methods of DNA fingerprinting are under continuous and rapid advancement within the scientific community, we are require continuing support for development of the most efficacious system for each new species to which population genetic diversity measures are applied. Most particularly, we will be expanding our efforts to examine plant population genetics. Plant work is being done primarily by Dr. Brian Keene, supported on fellowship though Interagency Agreement with Oak Ridge Institute. We are also developing an expanding battery of VNTR probes, such as PCR generated synthetic tandem repeat (STR) probes. We intend to adapt the new non-isotopic probe labeling techniques for use with our fingerprinting methods, which would avoid the use of radioisotopes, thus providing the advantages of standardization due to a long probe shelf-life and portability of methods to laboratories not equipped or certified for radioisotope usage.

We also will require continuous statistical support in order to tabulate and analyze data generated as each new population and species is examined and to continue to develop and refine the statistical methods required. This currently concerns characterizing the variability inherent in the DNA band visualization technique itself, in order to properly account for this source of uncertainty in the final population analysis. In addition, each new species examined presents a unique set of banding patterns to be analyzed, and these analyses also need to take into account characteristic higher-order population dynamics, most notably differences in breeding strategies. (This is especially true for plants that reproduce vegetatively as well as sexually).

We are developing liaisons with field ecologists who are experienced with and possess detailed knowledge of each relevant population. Much of this is inhouse, as our EPA colleagues are a valuable resource of talent. When appropriate and feasible, extramural collaborations will be formalized as Cooperative Agreements. This will provide detailed expertise and assistance in field sample collection.

We have also established a fruitful collaboration within the SERDP community. We are working with Dr. Mike Barcelona, Principle Investigator, and Mr. Mark Henry, site manager, of NCIBRD (National Center for Integrated Bioremediation Research and Development), to assess populations of animals and plants from Wurtsmith AFB, a DoD/National Environmental Technology Demonstration Program Facility. With their assistance, we have collected samples from several populations of bullhead catfish, amphibians and plants. These samples are presently being fingerprinted in the laboratory as a preliminary sampling. We will be returning to Wurtsmith for additional sampling and ecoassessments during the coming year. This collaboration provides a unique opportunity to correlate our fingerprinting results with the extremely well documented stressor history of the Wurtsmith environments and to demonstrate the efficacy of our methods as a monitoring tool as the remediations at Wurtsmith progress.

We are actively seeking additional opportunities to apply our method in field situations as a resource management tool. We expect these fingerprint measures of population genetic diversity to directly support the conservation efforts of DoD/DOE by providing assessment tools for monitoring, protecting and rehabilitating natural ecosystems, through SERDP as well as possible applications through other programs such as the Legacy Resource Management Program of DoD.

8. Expected Payoff:

The project will incur at least four major benefits to military ecological resource managers in DoD (and the public sector):
1) It will provide baseline data to assess the ecological impact of military activities, and thus will assist in planning remedial intervention and resource management decisions.
2) It will provide a quantitative means to document the ecological state of the areas impacted due to military activities.
3) In terms of impact, (cost/time/efficiency/capability) it will provide means of documenting the cost effectiveness of ecological interventions.
4) It offers significant possible improvements in terms of timeliness of the ecological assessment process.

9. Milestones/Accomplishments:

1. Field trips to collect plant and animal species from Wurtsmith AFB	11/95
2. Fingerprint method development for additional species, i.e. stonerollers, creekchub, green and leopard frogs, cat tails, blackberries	03/96
3. Analysis of plant and amphibian populations from Wurtsmith AFB	06/96
4. Continued data analysis, methods improvement, statistical interpretation and correlation with additional ecoindicators ongoing with increased emphasis	12/97

Manuscripts:

"Extremely RAPD Fingerprinting: a Versatile Tool for Population Genetics", Lattier et al., in press.
"Effects of Environmental Impacts on the Genetic Diversity of Brown Bullhead Catfish Populations", Silbiger et al., in preparation.

"RAPD Fingerprinting for Paternity Determination in Voles", Gordon, et al., submitted.

Results have been presented each year at the Society for Environmental Toxicology and Chemistry International Meeting.

10. Transition Plan:

We anticipate the development of a set of user-friendly, standard methods for monitoring population robustness that could be transferred to the individual end user or to centralized facilities which would run service samples for the end users. We expect these methods to be potentially marketable via a CRADA.

11. Funding: $(K)

FY93	FY94	FY95	FY96	FY97	TOTAL
200	200	0	190	200	790

12. Performers:

U.S. Environmental Protection Agency, National Exposure Laboratory - Cincinnati, Annette C. Roth, Ph.D.; Denise Gordon, M.S., Thomas Wessendarp, M.S., Oak Ridge Institute for Science/Education by Interagency Agreement, David L. Lattier, Ph.D., Brian Keene, Ph.D., Manju Garg, Ph.D., Tony Leonard, M.S., Department of Environmental Health, University of Cincinnati, by Cooperative Agreement until 10/01/95. Vicki Hertzberg, Ph.D. (Statistical Methods), DynCorp, Inc. by inhouse contract, Richard Silbiger, Ph.D., National Center for Integrated Bioremediation and Development, Mike Barcelona, Ph.D., and Mark Henry, M.S.

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14. Keywords:

DNA Fingerprinting, Ecological Monitoring, Genetic Diversity Measures, Heterozygosity Indices, Polymorphism, Population Genetics

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (Systemic, Genetic, Immune and Reproductive Toxicity Evaluation of Munitions-Impacted Terrestrial and Aquatic Fauna)

3. **Agency:** U.S. Environmental Protection Agency

4. **Laboratory:** Environmental Monitoring Systems Laboratory, Cincinnati, Ohio

5. **Project ID:** #244

6. **Problem Statement:**

The DoD has concerns about the potential ecological consequences associate with the contamination of soil and water with explosives and intermediates and by-products of explosives and other chemicals associated with munitions production and testing. Nitroaromatic munitions compounds and their by products e.g., 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene (DNB), tetryl (TET) are frequent contaminants at DoD facilities. These compounds are degraded by both anaerobic microbiological action as well as via chemically driven (e.g., photolysis, hydrolysis) decomposition processes. The propensity for these contaminants to enter ecological food chains and to bioaccumulate and to produce effects in wild terrestrial and aquatic is not well understood. Thus, at this time DoD is unable to conduct scientifically defensible, risk based assessments of the potential impacts of this class of ubiquitous chemicals on ecological resources (e.g., native feral plants and animals).

This project will assist DoD in developing a quantitative data base for the assessment of ecological risks associated with nitroaromatic munitions and their by products via the development of biochemical markers of exposure for ecologically important species. These biomarker data will be evaluated, and the changes will be correlated with existing ecological resources in impacted and reference sites. The results will be used in a diagnostic mode to assess the impacts of the munitions contaminants, to prove or disprove the cause-effect relationships, and to guide cleanup and restoration activities. The project effort will emphasizes the definition of assessment and measurement endpoints, their interrelationships, and the characterization of risk across various levels of ecological organization as outlined in the USEPA's *Framework for Ecological Risk Assessment.*

7. **Project Description:**

Goal: 1) To apply biomarkers (physiological, biochemical and molecular changes in aquatic and terrestrial organisms), as tools to assess and monitor impacts of defense-associated chemical production and applications, (e.g. munitions manufacturing, open detonation and open burning,

decommissioning and de-arming chemical agents, fuel refining and storage, machine de-greasing wastes, and chemical by-products) on sensitive aquatic and terrestrial fauna at selected DoD facilities; and 2) to establish patterns of biomarker changes, via comparative studies of native fauna in contaminated and reference sites, that are useful for demonstrating the existence or nonexistence of ecosystem level impacts from these materials, as which appear to be predictive of decrements n the status of the ecological resources. This project will fall in the category of basic (biomarker development) and applied (biomarker using risk assessment).

Previous Efforts/Accomplishments: The scientific staff at the U.S. EPA Ecological Exposure Research Division (EERD), National Exposure Research Laboratory (NERL), have extensive training, hands-on experience, and expertise in the areas of research that are required to carry out the proposed project successfully. They have a continuous record of peer-reviewed publication in research on biomarkers. In the past two years, and EERD scientists in collaboration with scientists form the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM), APG, MD and the Kirksville College of Osteopathic Medicine, Kirksville, MO have developed toxicity data for TNT and a series of its by-products (e.g., TNB, DNB, and TET) using small mammals (e.g., field mice and shrews). In addition, EERD scientist have discovered that nitroaromatic munitions compounds from chemical reaction products (adducts) with blood proteins and DNA in exposed animals. These adducts can be used to quantify the actual exposure of feral animals to these chemical contaminants. EERD has developed a cooperative agreement with the Department of Toxicology and Pharmacology, University of Louisville, Louisville, KY and this collaboration has developed new analytical procedures for assessing nitroaromatic adducts for exposure assessment. In addition, EERD has supported through the DOE Oak Ridge Institute of Science and Engineering (ORISE) Program, Oak Ridge, TN, two post-doctoral fellows who are developing ultrasensitive approaches for DNA (post-labeling) and protein (liquid chromatography-mass spectrometry) for screening wild animals for exposure to low levels of munitions chemicals.

Technical Approach: 1) The field samples will be collected at the SERDP demonstration site at the Volunteer Army Ammunition Plant (VAAP), Chattanooga, TN. U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM), Aberdeen Proving Ground, MD will assist EERD with the collection of feral mammals using live traps or the field evaluation of exposure using biomarkers. The U.S. Army Environmental Research Division will assist in determining the level of contamination at the animal trapping locations. In addition, The Nature Conservancy, Nashville, TN, has provided a list of fauna that have been identified at the VAAP as well as providing information on locations of species. Trapping site have been selected on the basis of animal census data and on soil contamination gradients which are located in strategic proximity to ecologically appropriate reference site(s). 2) The contaminated and reference sites will be inventoried and lists of ecological assets will be compiled. Suitable measurement endpoints will be selected on the basis of the biomarker methods available and on the ecological resources to be monitored. 3) The biomarker profiles of selected wildlife will be compared in the contaminated and impacted sites and referenced against the status of the ecological assets. 4) Biomarkers that appear useful as predictive of ecosystem impacts will be identified for future assessments at other DoD facilities.

Laboratory studies necessary to support the verification of field results will accompany the field studies.

Unique Assets Offered: EERD offers numerous assets and capabilities: 1) A highly qualified research staff including a staff of Ph.D. level scientists (ecologists, toxicologists and biologists) with substantial records of peer-reviewed publication. 2) State-of-art laboratory instrumentation as well as significant and proven experience in field sampling, sample preservation, transport and logistics. 3) A modern, accredited animal research facility uniquely equipped and a staff experienced in handling animal husbandry for a variety of terrestrial and aquatic species. The Division has developed breeding colonies of terrestrial (field mice, voles, and shrews, invertebrates,a nd plants) and aquatic (fish, tadpoles, invertebrates and plants) organisms. 4) A fully staffed aquatic research facility with a wide range of aquatic ecotoxicological and bioassessment capabilities.

Innovative Elements: This research is innovative in that, typically, biologically derived information about ecological impacts have been limited to traditional evaluations of community structure and the direct measurement of tissue residues. Biological markers provide predictive and diagnostic information not only to detect exposure, but also to detect early effects of these exposures and to identify causes. Biomarkers can focus efforts where they are most needed for the protection of wildlife; e.g. on contaminants that are biologically available, which bioaccumulate, and which are biologically active (e.g. toxic).

Relationship to DoD Environmental Objectives: This project will directly support the Conservation Strategy by providing quantitative indicators of the health status of the impacted fauna, leading to enhanced ecological risk assessment. The DoD is in the process of establishing the toxicological and ecological data base for determining the potential environmental effects of munitions chemicals that have been discharged in the environment over previous years.

Technical Issues to Overcome: Only one of the original technical impediments remain. The selection of appropriate site(s), coordination with other research organizations dealing with the site studied has been resolved. Likewise, the selection appropriate biomarkers has been completed as protein and DNA adducts will be the focus of all future exposure assessment research for this project. The last issue, i.e., the development of systematic methods for using biomarker data to assess and predict ecosystem impacts will be addressed in the analysis of the exposure data collected of the laboratory and field studies over the next two years.

8. Expected Payoff:

The project will provide five major benefits to DoD: 1) It will provide a quantitative means to prove or disprove cause-effect relationships between munitions byproducts contaminated and ecological effects. 2) It will provide baseline data to assess the ecological impact of munitions activities, thus assisting in planning remedial intervention. 3) In terms of impact, (cost/time/efficiency/capability) it will provide means of documenting the cost effectiveness of ecological interventions. 4) It offers the possibility of significant improvements in the timeliness

of the ecological assessment process. 5) It will assist in evaluating/reestablishing genetic and biodiversity particularly of sensitive and endangered species at impacted area.

9. Milestones/Accomplishments:

FY 1996 Milestones:

1. Identification of sites for trapping *Peromyscus*, and Cryptotis at VAAP locations. 03/96

2. Initiate field collection of animal/blood/tissue samples and initiate pilot laboratory support analysis as appropriate for field samples. 04/96

3. Field sample analysis for biomarkers detection and quantitation (the blood and tissue samples collected from the field will be analyzed for hemoglobin and DNA adducts). 06/96

4. Initiate studies in data analysis; including data reduction and statistical analysis, approaches utilize biomarker data in ecological risk assessment by comparing field sample data with the in-house biomarker data that was obtained by treating rodents with known concentrations of the test chemical as well as the contaminant levels at the site from where the animals were trapped. 09/96

In the first year, all funding instruments (two interagency agreements, one on site contract, and two cooperative agreements) were developed and executed in the June to September, 1994 time frame. All funds were transferred to the participating agencies. Protocols for research, including quality assurance plans, have been developed for all projects and laboratory phases of all projects that have been initiated. The initial toxicology study with 2,4,6-trinitrotoluene (TNT) in white footed mouse (*Peromyscus leucopus*) has been completed and data analysis is in progress. Toxicity studies on 1,3,5-trinitrobenzene (TNB) in white-footed mouse (*P.leucopus*) and the least shrew (*Cryptotis parva*) have been completed and that analysis is being completed. The calculated no observed adverse effect level (NOAEL) of TNB in *Peromyscus* was 20.8mg/kg/day (combined sexes). At higher doses (100mg/kg/day) TNB induced testicular degeneration, erythroid cell hyperplasia (spleen), and increased spleen weights. In *C. parva*, the NOAEL was 10.7 mg TNB/kg/day. j At higher doses (40 mg TNB/kg/day, the kidney and splenic effects were similar to those observed in *P. leucopus*. Blood protein adducts of these two trinitroaromatic munitions compounds have been observed and appear to be suitable candidates for exposure biomarkers of munitions byproducts.

Research agreements (e.g., contracts/interagency agreements) were made with ICI America, who are the contractors for the Volunteer Army Ammunition Plant (VAAP), Chattanooga, TN, through Army Environmental Center, Aberdeen Proving Ground, MD< for collection of live trapped rodents from the contaminated sites at VAAP. Currently the health safety protocols are being prepared. Upon approval of protocols by the safety officer, the actual sample collection will be

initiated. The sample collection will be done in conjunction with the Nature Conservancy at Nashville, TN., or CHPPM. Nature Conservancy has developed a list of fauna present at VAAP.

Maria T. Pinorini-Godly, Ph.D. and Achal Garg, Ph.D., were hired as post doctoral fellows through Oak Ridge National Laboratory, Oak Ridge Institute for Science and Education. Dr. Pinorini-Godly is working on the identification and characterization of hemoglobin adducts at the University of Louisville, Department of Toxicology and Pharmacology with Dr. Steven Myers. They have recently developed an ultrasensitive method for the identification of protein adducts formed by nitroaromatic munitions compounds. This method will be utilized in the field studies scheduled for this summer (see above). Dr. Garg has started his work on the characterization and quantitation od DNA adducts using an ultrasensitive ^{32}P-post-labeling technique (in-house at EPA). A manuscript detailing the toxicity of TNT and TNB will be prepared upon completion of the data analysis.

Dr. Sylvia Talmadge (ORNL) has completed the preparation of Ecological Criteria Documents for TNT, TNB, and DNB. Three additional documents will be prepared. These documents will help DoD to place the exposure information developed in this project for nitroaromatic munitions compounds into a risk perspective.

10. Transition Plan:

DoD/DOE has assisted in the selection of priority site(s) for the study and for the chemical characterization of contaminating agent(s) via a survey of prior DoD/DOE funded and completed descriptive and analytical efforts. The target species will be identified in the impacted ecological community, and a control population will be identified at appropriate reference site(s). The testing chronology will be defined and coordinated with restoration activities. Biomarker matrix endpoints will be identified based on expected site impacts and va experience with previous industrial studies. IN start-up phase validation of the sampling strategy, validation of assays, establishment of baseline reference ranges and quality assurance measures will be verified and reported to DoD. In the initial comparative phase the sampling, assay data collection, and comparative analysis of impacted versus reference sites will be conducted and reported to DoD and the feedback will drive corrective actions(s) in conformance with quality assurance standards. Finally, the evaluation phase will cover statistical analysis, peer review and preparation of a final report to DoD. All of the above phases will require close consultation and coordination with DoD personnel in charge of the sites studied. Such communications will be both verbal and written.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	800	0	400	1,200

12. Performers:

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14. Keywords:

Ecological Biomarkers, Ecological Risk Assessment, Ecological Exposure Assessment, Munitions, Site Assessment, Wildlife Protection

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Conservation

2. **Title:** Ecological Modeling for Military Land Use Decision Support

3. **Agency:** U.S. Department of Energy

4. **Laboratory:** Oak Ridge National Laboratory (ORNL)

5. **Project ID:** #758

6. **Problem Statement:**

U.S. Department of Defense (DoD) and U.S. Department of Energy (DOE) lands are subjected to a wide variety of uses ranging from military training to hazardous waste disposal to timber production. Nevertheless, these lands are often the last large natural areas in otherwise developed environments. As such they represent valuable resources for preserving the biodiversity of their local regions. Currently, there is no unifying framework for managing these lands that provides decision makers with a consistent approach to balancing the goals of DoD and DOE missions with the need for resource conservation. However, several projects within the SERDP Conservation thrust area are working together to develop a decision support system that will provide decision makers with a set of tools that can be used to evaluate the environmental consequences of various land uses. This document describes the ecological modeling task being conducted by Oak Ridge National Laboratory. Ecological models are key components of this overall system.

We will develop and demonstrate advanced computer-based models to predict incremental and cumulative impacts of agency activities on valued habitat and sensitive species and to find solutions that maximize mission-oriented use of the land while sustaining long-term ecological diversity. These models characterize resources in a risk assessment framework to provide support for DoD and DOE land management that is applicable to levels of organization ranging from species to ecosystems. By risk assessment, we mean to estimate the probability of undesirable (or desirable) outcomes of land management activities in a spatially explicit fashion. The models will provide agency decision makers with tools for evaluating the effects of alternative land management activities on natural resources. The models will be useful to land/facility managers and planners for addressing questions such as: What training activities can occur without risking an impact to sensitive species or habitats? Across a set of potential sites, where would an activity best be placed to minimize the effects on biotic resources? What remedial actions would provide the maximum conservation benefit? What are the impacts on habitats or species of changing the frequency or intensity of training exercises at a site?

7. Project Description:

We propose to develop innovative spatially-explicit decision models that will be used to assess the impact of DoD and DOE activities on natural resources. The models will focus on the loss/alteration of habitat and the resulting impact on biodiversity. Agency land-use activities will be characterized using a common set of parameters (magnitude, frequency, areal extent, spatial distribution, predictability) that can be applied both to alternative activities and to different levels of the same activity. This approach permits the incremental and cumulative effects of diverse activities, such as training, roadbuilding, military maneuvers, construction of runways, timber harvests, and environmental restoration, to be evaluated. Evaluating the risk posed to habitats and species is expressed as the probability of a decline or enhancement in the abundance of guilds of species (e.g., territorial migrant birds) or valued habitat types (e.g., wetlands, cedar barrens). Federal laws and executive orders protect such species and habitats, and their violation can stop or impair agency activities. Because the approach is generic, the models, given appropriate local parameters, can be applied to any site.

Model development will focus initially on case studies consisting of paired DoD/DOE sites where each pair is within the same physiographic region. The first case study involves development of models for sites in the ridge and valley physiographic region of the eastern deciduous biome. The Oak Ridge Reservation (ORR) and Ft. Knox respectively encompass 14,000 and 44,700 ha of eastern deciduous and coniferous forest. Large blocks of land have been cleared for low-level radioactive waste disposal areas on ORR while tank and artillery training at Ft. Knox (Ft. Knox's main mission) has denuded scattered blocks of land. Development of specific models for these two sites provides a set of tools that can be used at most DoD and DOE sites in the eastern third of the United States. With appropriate parameterization, the models may be used throughout the rest of the country wherever analogous vegetation types or guilds of species exist.

Our approach entails five components which integrate existing data, model development and demonstration, and risk assessment. It should be noted that other tasks within the SERDP Conservation thrust area are addressing some of the same issues in a fashion complementary to the ORNL effort. We are working closely with the organizations conducting those tasks to minimize duplication of effort and to enhance our own efforts. Specific examples of this coordination are included, where appropriate, in the following examples.

1) Quantitatively characterize land-use activities. A matrix of characteristics to describe land-use activities on DoD lands in terms of magnitude, frequency, areal extent, spatial distribution, predictability, and effects on habitat quality will be developed. For example, some types of troop training are low-intensity impacts that are dispersed throughout a site, whereas construction of an industrial facility is a high-intensity activity that occupies a limited area.

Some of this work is similar to efforts underway at Argonne National Laboratory (ANL) and the Corps of Engineers' Construction Engineering Research Laboratory (CERL) in the development of their IDLAMS project. In fact, IDLAMS will be the overall system into which our ecological models will be incorporated. However, IDLAMS work, to date, has focused on very different types of habitat, and does not currently consider the eastern deciduous forest biome. Rather than

duplicate efforts, we have agreed with ANL and CERL to restrict our efforts in this area to the level of effort necessary to provide the information needed by our models for eastern deciduous forest species. The net result will be that the overall set of tools will include our products for the eastern deciduous forest and those developed by ANL and CERL for grassland and oak savanna ecosystems.

2) Develop a land-cover change risk model. A spatially-explicit, land-cover change model will be developed to simulate potential changes in or loss of individual cover types in response to the land-use activities. Inputs to the model will include the matrix of parameters describing land-use activities, and gridded (digital raster) maps of site characteristics, such as present land cover, slope, aspect, soils, etc. The model will simulate the impact of land use activities on land cover. The model will be probabilistic and include stochastic aspects of the land-use activity (e.g., the frequency of training maneuvers) or its effects on the habitat (e.g., the degree to which a forest is damaged by artillery fire). Land-use activities that are relatively deterministic and depend on the suitability of the land (e.g., location of new runways). They are easily accommodated within a probabilistic model by setting the appropriate probabilities to 1.0 and fixing specified parameters. From the model, tables and maps of potential land-cover change due to land use activities will be produced for a particular site. The land-cover change projections will be developed for various scenarios of land-use activities and land cover patterns. Stochastic simulations with the model can be replicated many times and the results summarized statistically, thereby providing an estimate of the magnitude and range of potential effects. Most importantly, the stochastic but mechanistic nature of the modeling will allow us to quantify the probability of specific land-cover changes taking into account known uncertainties.

Again, this effort is complementary to IDLAMS efforts in grassland and oak savanna ecosystems. Our model will address eastern deciduous forest, which is very different in its response to various land uses. The net result is a set of tools that includes models for all three types of ecosystems; a more robust toolkit than if all three organizations focused on the same ecosystem.

3) Develop a resource-susceptibility model. The resource-susceptibility model will relate characteristics of species and ecosystems to land-cover patterns resulting from land-use activities, as projected by the land-cover change model. This resource model will match land cover characteristics (e.g., frequency of land cover types, abundance of suitable habitat, size of habitat patches, frequency of edges, corridors, etc.) to species and ecosystems characteristics (e.g., home range size, vegetation patterns). For example, activities that cause habitat fragmentation (e.g., tank maneuvers in new areas) are detrimental to species that require large blocks of contiguous habitat (e.g., forest-interior species). This model will be probabilistic to ensure its compatibility with quantitative risk assessment. Potential effects on species and ecosystems of no management, alternative land-use activities, environmental restoration, or natural events can be examined. The probability of an undesired or desired outcome (such as loss or increase of a population of interest) is estimated by Monte Carlo simulations of the models under particular scenarios and examination of the frequency distribution of outputs. The visualization that will accompany this spatially-explicit model will also permit managers to "see" the effects of alternative activities on populations of interest.

We are investigating the potential of other models being developed outside the SERDP program to complement the ongoing effort. If such models can be found, they will be incorporated into our efforts and into the final set of tools.

4) Use case studies to field test the modeling approach. Each model will be tested by applying it to field sites that have sufficient data to provide a sufficient test. At present, we plan to test the first set of models for effects of training plans on susceptible habitats and species at Ft. Knox. To the extent possible, existing land-use/land-cover and resource maps will be used, however some map development may be required.

5) Conduct risk assessment. As noted earlier, risk assessment provides a probabilistic evaluation of expected effects of various land-use scenarios. The previously described models will provide probabilistic outputs regarding the effects of scenarios on land cover, species abundance and distribution, and the abundance of valued habitat types. We are working with the developers of the IDLAMS to ensure that our models are consistent with the overall structure of IDLAMS and that the user of IDLAMS receives output in a format that is conducive to decision making.

8. Expected Payoff:

This research will provide a rigorous, quantitative method for conserving and enhancing biodiversity while conducting activities necessary for DoD and DOE missions. The results will include:

1) A general risk-based framework that can be used by DoD and DOE land managers and site development planners to analyze the potential impact of selected land-use activities on natural resources.

2) Case study results including projections of percent change in cover and distribution of habitats and species guilds for various land management and site development scenarios at the case study sites along with maps of potential risks to different land cover types under the specified land management scenarios.

3) A user-friendly version of the land-cover susceptibility and species-susceptibility models that could be applied at various DoD and DOE sites.

In addition to its use for management of natural resources, the proposed research is directly applicable to 1) planning for facility closures and realignment (e.g., identification of facility closures that provide the best conservation opportunities), 2) developing environmental restoration and waste management strategies, 3) supporting compliance with the Endangered Species Act, the National Historic Preservation Act, the National Environmental Policy Act, and the Executive Orders for Floodplains and Wetlands, and 4) developing integrated risk assessments that address cumulative effects.

9. Milestones/Accomplishments:

FY 1996 Milestones:

1. Test habitat models at Ft. Knox (e.g., cedar barrens, Henslow sparrow, and cerulean warbler).
2. Complete preliminary vegetation dynamics model for assessing impacts of training activities on land cover in an eastern deciduous forest ecosystem (e.g., Ft. Knox).
3. Complete preliminary population dynamics model for territorial migrant fauna (e.g., Henslow sparrow, cerulean warbler).
4. In coordination with staff at CERL, identify and prioritize additional guilds for which population dynamics models are needed.

FY 1997 Milestones:

1. Finalize vegetation dynamics model for eastern deciduous forest and transfer to IDLAMS.
2. Finalize population dynamics model for territorial migrant fauna and transfer to IDLAMS.
3. Complete preliminary population dynamics model(s) for highest priority guild(s) identified in FY 1996 (Milestone 4).

FY 1998 Milestones:

1. Finalize population dynamics model(s) begun in FY 1997 (Milestone 3).
2. Conduct field tests of vegetation dynamics and population dynamics models at DoD sites.

FY 1994 and 1995 Accomplishments:

1. We have developed a strategy to predict the impacts to species at risk from land use activities. This strategy builds upon a GIS model of existing land cover and expected land use activities, vegetation dynamics models, and models of species at risk (see Section 8, Expected Payoff, Item 1).

2. We completed and tested a GIS-based model for predicting the location of cedar barrens--an important habitat type in the southeastern United States. The model was tested at the Oak Ridge Reservation and has been applied to Ft. Knox. In addition, we have coupled this model with a predictive model of tank training areas to provide a visual means of determining where conflicts between tank training and cedar barrens habitat are likely to occur. These models are part of the case study component of our task (see Section 8, Expected Payoff, Item 2).

3. We have also developed GIS-based models for predicting the location of habitat for territorial migrant fauna (i.e., cerulean warbler and Henslow sparrow). Both of these birds are important territorial migrant species at Ft. Knox and other DoD and DOE locations.

4. At the urging of SERDP staff, ORNL initiated a series of coordination meetings with ANL and CERL. The result of these meetings is a documented understanding of the means to integrate the efforts of all three organizations as well as input from other, non-SERDP-funded projects.

10. Transition Plan:

User-friendly codes of the models and land-use management framework developed in this proposal will be transferred to DoD and DOE land managers and site development planners.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	500	260	340	600	400	1,900

12. Performers:

Ecological model development will be performed by Oak Ridge National Laboratory, Batelle Pacific Northwest Laboratory, and the University of Wisconsin. Field testing will be conducted at Ft. Knox and other DoD and DOE facilities as appropriate.

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14. Keywords:

Biodiversity, Land Use, Habitat, Ecological Risk, Site Development Planning, Species Guilds

TABLE XXI
FY 1996 GLOBAL ENVIRONMENTAL CHANGE PROJECTS

TABLE XXI FY 1996 GLOBAL ENVIRONMENTAL CHANGE PROJECTS	Funding $(K) FY96	ID Number	Page Number
Atmospheric Research			
Atmospheric Remote Sensing and Assessment Program (ARSAP) (DOE)	725	470	GEC-2
Ocean Research			
Acoustic Monitoring of Global Ocean Climate (ARPA)	2,000	286	GEC-13
Global Environmental Change Total	**2,725**		

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Global Environmental Change
2. **Title:** Atmospheric Remote Sensing and Assessment Program (ARSAP)
3. **Agency:** U.S. Department of Energy & Department of Defense
4. **Laboratory:** Sandia National Laboratories (SNL) and Naval Research Laboratory (NRL)
5. **Project ID:** #470
6. **Problem Statement:**

This is a joint DoD/DoE project to investigate, understand, and assess global atmospheric change. The program will develop improved measurements and understanding of the earth's atmosphere and its response to global change. It will utilize and augment 1) existing DoD space-based sensors of the middle and upper atmosphere, 2) ongoing theoretical modeling activities, and 3) will develop DoE sensors and measurement techniques for observing the lower atmosphere. The effort will consist of the application of unique DoD/DoE ongoing research on environmental issues through measurement of key observables, validation of models, and assessment of evidence of global atmospheric change. This DoD/DoE activity will be coordinated with other national environmental programs such as the US Global Change Research Program (USGCRP).

Both natural and anthropogenic agents contribute to global atmospheric change. Subtle variations in the solar irradiance and the periodic injection of dust and gas into the lower stratosphere by volcanoes can profoundly alter climate. The increased emission of CO_2, methane, CFCs, and pollution resulting from human activity, enhances the natural atmospheric greenhouse effect and depletes the ozone layer. The nature of atmospheric change depends on the region of the atmosphere:

Atmospheric Region	Issues	Characteristics
Lower	Climate	Global warming, UV increase
Middle	Ozone, UV shielding	Ozone depletion, atmospheric cooling, climate impact
Upper	Atmosphere circulation	Global cooling, potential coupling to biosphere

There is ample evidence for global atmospheric change already. The steady increase in atmospheric CO_2, methane and CFCs is well documented. Global warming of the troposphere has been observed over the last century. Mid-latitude depletion of the ozone layer and the seasonal Antarctic "ozone hole" result form the emission of CFCs. In the middle and upper atmosphere,

there is evidence of a general cooling (at a rate more rapid than predicted by current models) and an increase in the occurrence of polar mesospheric clouds.

7. Project Description:

DoD - MIDDLE AND UPPER ATMOSPHERE

Because of the strategic decision to de-emphasize global change in SERDP, the Atmospheric Remote Sensing and Assessment Program (ARSAP) has fashioned its plan to achieve an orderly conclusion of the program and transition to sustaining science programs. These science programs will continue using hardware and capabilities developed in SERDP. The portion of ARSAP concerned with ozone depletion has established the following exit criteria.

- Completion of the test and launch of the Orbiting Ozone and Aerosol Monitor (OOAM) mid-latitude stratospheric sensor.

- Completion of a functioning, automated data processing and archiving system for Polar Ozone and Aerosol Monitor (POAM), OOAM, (and the POAM follow-on being funded from other sources) geophysical data. This system to be available to the research community via DoD communications networks. Naval Research Laboratory (NRL) science operations of these systems will be sustained by NRL/Office of Naval Research (ONR) support.

- Completion of two ground-based microwave sensor elements for the Network for Detection of Stratospheric Change plus one back-up/test system. Systems to be operated by NRL with NASA sustaining support.

- Conduct science analysis of all data acquired during FY-95.

Descriptions of each part of ARSAP are given below:

<u>Millimeter-wave Atmospheric Sounder (MAS)</u>

In FY95, the analysis of the MAS data obtained during ATLAS 1, 2, and 3 flights was essentially completed, and six papers were submitted for publication in Geophysical Research Letters. In addition, using SERDP money, arrangements were made for the indefinite storage of the MAS instrument at NRL. In FY96, emphasis will shift to writing detailed ozone and water vapor validation papers. According to current plan, the MAS project will be phased out after FY96, because no more ATLAS missions appear on the shuttle manifest. Owing, in large part, to the generous financial support of SERDP through the ARSAP program, the MAS experiment can be considered a success which has greatly increased our understanding of the distribution of trace constituents in the middle atmosphere.

Orbiting Ozone and Aerosol Monitor (OOAM)

The delivery date for the OOAM flight hardware has been extended to March 1996. Activity on this project will center upon monitoring the final fabrication, and planning and aiding in the execution of the instrument characterization tests, which must be conducted before instrument delivery. We also need to analyze the data obtained in these instrument characterization tests to ensure that the instrument is performing to specifications and that its operation is well understood before integration onto the STEP 4 spacecraft. Finally, during the year we will work with TRW on the integration of OOAM onto the SPOT 4 spacecraft.

POAM/OOAM Analysis

The POAM II instrument was launched on 26 September, 1993 and is still operational. Owing to the support of SERDP, the POAM II experiment is returning excellent data and is considered a complete success. The unique data set obtained from POAM has enabled us to document the dissipation of the 1993 ozone hole, and the formation and dissipation of the FY94 ozone hole in unprecedented detail. One paper has now been published in Geophysical Research Leters, and another has been accepted for publication. A third paper, describing the POAM II instrument, has been submitted to the Journal of Geophysical Research.

FY96 funds will be used to continue to operate the POAM II satellite instrument, and to help reduce and analyze the data obtained in the experiment. In addition, work will continue in FY96 on improving the POAM retrieval algorithm, especially the retrieval of ozone below about 17 km and water vapor and nitrogen dioxide throughout the stratosphere.

The OOAM engineering model is now complete and fabrication of the flight model is underway. Optical filter measurements are now underway. Instrument delivery is scheduled for November 1995 and the launch of OOAM is scheduled for August 1997.

Ground-based Water Vapor Millimeter-Wave Spectrometer (WVMS)

The first and second WVMS instruments (WVMS-1 and -2) are now in the field (Lander, New Zealand, and Table Mountain, CA) and are operational. WVMS-3 is now being deployed at Table Mountain, CA (TMO) where it will undergo side-by-side tests with WVMS-2. It will then be shipped to the NDSC Facility at Mauna Loa, to begin official NDSC operations, late this year. In addition, WVMS-4 will be deployed late this CY first at TMO for testing, then at Thule, Greenland, for NDSC operations. The FY96 SERDP money will be used to partially support these hardware activities, which will occur early in the FY.

FY96 will be a transition year for the WVMS program. With the completion of the tasks described above, we will have used SERDP funding to put in place an effective network of ground-based middle atmospheric water vapor measurements. The measurements provided by these instruments have clearly given the highest quality middle atmospheric water vapor data which has ever been obtained, and they will be a very important part of the NDSC program.

After FY96 (in fact, mid-way through FY96), the instrument fabrication, and extensive modification stage of the program will come to an end, and the WVMS project will center upon maintenance of the instruments in the field and analysis of the data acquired with the instruments.

Advanced Research and Global Observation Satellite (ARGOS)

The two SERDP-supported experiments on the ARGOS satellite form the NRL Space Science Division, HIRAAS and GIMI, have made good progress and are now starting integrated testing of subsystems and systems. Problems with a critical part in the spacecraft electronics for the ARGOS satellite have forced an overall program delay, so that delivery of the NRL experiments is now March 1996, and the anticipated launch date is now March 1997. Although some of this delay was needed by the experiment teams to solve their own problems, the stretch out has forced the experiment groups to reduce the size of their teams, and slow down their own schedules, in an attempt to minimize costs while maintaining a strong engineering capability through delivery to the spacecraft contractor and subsequent testing before launch.

The plan for the ARGOS Coordination Office has always been to reduce in size after completion of the experiments, but to maintain some presence through experiment delivery and possibly through launch to handle issues of management, hardware, and software common to the NRL Space Science Division experiments.

High Resolution Airglow/Aurora Spectrograph (HIRAAS)

The HIRAAS experiment requires support for scientists and engineers during the stretched-out schedule, since FY96 now includes the critical testing and calibration of the instruments. This is an especially severe problem for HIRAAS because the experiment consists of three separate instruments that operate together but must be prepared, tested, and calibrated separately.

Global Imaging Monitor of the Ionosphere (GIMI)

The Ultraviolet Measurements Group is developing the GIMI experiment for flight on the ARGOS satellite in 1997. The objectives of GIMI relevant to SERDP are to: demonstrate global remote sensing of the day and night ionospheres, by wide-field imaging in ionospheric emission lines; demonstrate remote sensing of neutral atmosphere (O_2,N_2) at night by observations of the occultations of UV-bright stars by the atmosphere; and measure and monitor atomic nitrogen in the middle atmosphere by observations of NO nightglow emission.

These objectives support the SERDP thrust area of Global Environmental Change, by monitoring changes in temperature and composition of the upper atmosphere which can be induced by greenhouse gases and other pollutants introduced into the lower and middle atmosphere.

Middle Atmospheric High Resolution Spectrograph (MAHRSI)

MAHRSI was a highly successful experiment. It's flight on CRISTA SPAS resulted in the first global measurement of mesospheric OH. Reflight of the instrument will provide measurements

of the atmosphere under conditions very different from the first flight, giving the second flight high scientific value. The experiment has firm commitment for a reflight as part of an international collaboration. DARA and DASA require a MAHRSI preintegration test at KSC in October 1996. To prepare for the test we must begin implementation of hardware and software changes to the telemetry interface. The changes are necessary because of the upgrade of the ASTRO-SPAS in progress as part of preparation for the Space Station mission. The science goal of the changes is to increase by a factor of two the measurement horizontal resolution.

DOE - LOWER ATMOSPHERE

Given the decision to phase out the GEC pillar, DOE's phase out strategy is to maximize the benefit to SERDP and to the broader US Global Change Research Program by: (1) completing the development of the four key instruments cited below; (2) focusing the two remaining missions on cloud heating and satellite calibration issues at mid-latitudes, with special attention to the recently observed 'enhanced short-wave absorption'--an effect which can have a dramatic impact on our understanding of atmospheric heating; and (3) insuring that the overall system is as close to operational as possible, so that it can readily be picked up by future users.

The DOE program is a critical complement to its Atmospheric Radiation Measurement (ARM) program. The ARM ground sites are heavily instrumented with DOE Cloud and Radiation Testbed (CART) instrumentation as well as from other government programs. However certain key quantities must be measured in the atmosphere. These quantities include the solar and thermal fluxes at various levels in the troposphere, and especially at the tropopause; properties of cloud tops and layered clouds; and the distribution of upper tropospheric water vapor. Furthermore these measurements must be made up to the tropopause (20 km in the tropics) and for multiple days so as to sample diurnal and synoptic effects. These combined altitude-endurance measurements are beyond the capability of manned aircraft and are best met using unmanned aerospace vehicles (UAVs) that are now under development by industry.

Therefore we are developing the necessary UAV-compatible instrumentation and flying them on UAVs to demonstrate and validate the measurement techniques and to obtain early scientific data. In implementing this, we are following a three-phased approach, taking maximum advantage of the increasing instrument and UAV capabilities as they are developed by ARSAP and by industry. The first phase concentrates on demonstrating the needed accuracy in radiative flux profiling using a low-altitude UAV under clear sky conditions. This phase was completed in a highly successful series of flights in April, 1994 and constitutes the first-ever climate measurements from a UAV. The second phase then extends these measurements to mid-altitudes (40kft--the mid-latitude tropopause) and to cloudy skies. It depends critically on the ability to make coordinated measurements from two aircraft, one above and one below clouds and on the new UAV-compatible instruments being developed in this program; i.e. a novel net flux radiometer, an imaging cloud radiometer, a cloud detection lidar, and a small interferometer. This phase is well underway--instrument development is more than 75% complete, coordinated flight has been successfully demonstrated in engineering flight tests (Aug, 1995) and in a major series of 12 scientific flights (Sep-Oct) which have provided a unique data set for testing and refining our understanding of solar absorption in cloudy skies. The FY96 activities discussed below will

bring this second phase to a successful conclusion. The third and final phase was intended to provide the full altitude capability (65 kft) needed for the tropics and extends the measurements to other scientific locales and to instruments now under development by the Science Team. This third phase will be sacrificed because of the early termination of the Global Environmental Change (GEC) pillar.

Specifically, two missions will be conducted and/or completed in FY-96; and the program transitioned to DOE for scientific operations. The two missions are:

1. The ARESE (ARM Enhanced Short-wave Experiment) mission (Sep-Oct 95), used highly accurate radiometers aboard two coordinated aircraft, one over and one under clouds, to test and improve our understanding of the absorption of solar radiation in cloudy skies, including the recent hypotheses of significantly enhanced solar absorption. If confirmed, 'enhanced absorption could have a significant impact on current climate and weather models as well as on the algorithms used to retrieve atmospheric data from satellite measurements. This mission also marks the maiden scientific flights of the Cloud Detection Lidar developed under this program (it was test flown in an engineering flight in Aug).

2. High Altitude Cloud Properties/Satellite Calibration missions use the SERDP developed imaging cloud radiometer (MPIR) aboard a 45,000 foot capable manned aircraft (Spring 96) to (a) test and refine various algorithms for retrieving cloud properties (reflectance, ice/water phase, and droplet size) from remote sensing data; and (b) provide indirect calibration for the currently uncalibrated visible sensors on existing weather satellites, thereby greatly improving the utility of these satellites for climate studies.

The SERDP work will be brought to a successful conclusion by integrating four SERDP developed instruments into a single UAV payload (Aug 96) and transferring this capability to DOE for scientific operations commencing in Sep/Oct 96. The four instruments measure cloud geometries, cloud optical properties, and upper atmospheric water vapor. They will be integrated along with supporting systems, into a payload for the Altus, a 45,000 ft-capable UAV that is derived from the highly successful Predator now used for defense applications. This will provide both the DOE climate community and the DoD weather community with a robust payload/UAV combination for conducting future missions. The program will then be officially transferred to the DOE, with DOE funded scientific missions scheduled to commence in Sep/Oct 96.

Ultra Violet Remote Sensing Database Systems (UVRS DBS)

The initial version of the nightside ion/neutral density retrieval code for the analysis of ultraviolet (UV) limb scanning data is now available, resulting in significant improvements over conventional analysis techniques. Work has begun on the transfer and application of software for the development of empirical models of thermospheric composition, temperature, and winds. These models form the core of the software for inversion of UV remote sensing data and conversely, the composition measurements by SERDP-supported systems will form the basis for new empirical models. These models will form the basis of thermospheric modeling and data analysis for the foreseeable future to be supported within the Navy RDT&E core program.

MAP Theory

The principal activities in the MAP Theory group currently cover studies of the chemical, dynamical, and radiative processes in the stratosphere, mesosphere, and lower thermosphere. The goals of MAP theory research include the identification and understanding of those processes which control (1) the distributions of 0_3 and IR active gases such as H_20, N_20, CH_4, $C0_2$, NO, and CFC'S, (2) the dynamical state of the middle atmosphere and the chemical/dynamical/radiative interactions between the middle atmosphere and troposphere, and (3) the physical/chemical coupling between the middle atmosphere and the thermosphere above. Summaries of progress in selected MAP research projects are included below.

Chemical/dynamical modeling of the stratosphere and mesosphere.
The NRL 2-dimensional chemical/dynamical/radiative model of the middle atmosphere, developed under SERDP, is being used to test parameterizations of planetary wave and gravity wave drag and corresponding horizontal and vertical mixing in the middle atmosphere. This study is using observed trace gases such as H_2O and CO from both UARS and ground-based stations as indicators of advective and diffusive transport. This work strongly suggests that horizontal mixing plays a much more important role in the mesosphere than previously believed. Summers presented this work at IUGG in early July. Recent work centers on the 2-dimensional model consists of incorporating equatorial dynamics in the model, primarily focusing on reproducing the observed stratospheric semi-annual oscillation (SAO). The model is also being used to study the effects which control the distribution and variability of high latitude NO and he presented early results at IUGG in July.

Atmospheric Dynamics Research

We are analyzing high altitude aircraft wind and temperature data for signatures of dynamical processes including gravity wave and planetary wave breaking and turbulence in the lower stratosphere and upper troposphere. This research suggests that most turbulence in the lower stratosphere is a result of gravity wave activity.

3-D Dynamics Model Development

We are developing a finite-difference, isentropic-coordinate, vorticity-divergence model to examine the basic evolution of potential vorticity in the atmosphere. The advantage of a finite difference formulation over a spectral one is primarily in the flexibility it provides for examining a variety of geometries. We have recently tested a multigrid solver on the sphere against known solutions. We are in the process of examining the accuracy of our advection scheme for cross polar flow.

8. Expected Payoff:

The radiation, water vapor, and cloud measurement capabilities will be a major tool in understanding radiation-cloud interactions. These uncertainties drive the magnitude of global warming response and impact policy decisions on energy-related emission and mitigation

strategies. The improved measurement capabilities are an important complement to the ARM program and serve as the basis for a future ARM-UAV program to be funded by DOE. This will be a unique capability for long endurance radiative heating measurements up through the tropical tropopause (20 km) and will allow 'indirect calibration' of satellite data, thereby greatly leveraging the use of existing weather satellites. These improvements can also provide the DoD with enhanced weather data, with redundancy in the case of satellite loss during critical operations, and provide improved infrared backgrounds for weapon system sensors. Representatives of both the Defense Meteorological Satellite Program (DMSP) and of NOAA have expressed interest in several of the instruments for weather satellite applications. The UAV demonstrations will be a key step in establishing these platforms as a "better, faster, cheaper" complement to satellite measurements.

The measurements of the upper atmosphere fill an urgent need for space-based atmospheric measurements during the 1995-2000 time frame. The NASA Upper Atmospheric Research Satellite (UARS) was launched in September 1991 and has a projected lifetime of 5-7 years and the Earth Observing System (EOS) atmospheric chemistry missions are scheduled for after the turn of the century. Thus, there is a gap which will be filled by this program during which policy decisions regarding global warming and CFCs must be assessed. Further, a continuation of this program complements the capabilities and global coverage of EOS allowing an uninterrupted series of measurements of the Sun/Earth/atmosphere system for two decades.

A significant benefit to this research activity is the cost savings realized by utilizing existing DoD and DOE observational and theoretical capabilities. Especially important is the leveraged costs of launching sensors into orbit. Existing data centers, Background Data Center (BDC) and Global Change Distributed Information System (GCDIS) will be used for data archiving and management.

9. Milestones/Accomplishments

Middle and Upper Atmosphere	
First O_3 space based observations	03/92
Space flight of POAM	09/93
3D Dynamical/photochemical model	09/94
ATLAS3 Shuttle Flight	10/94
MAS Failure Analysis Complete	03/95
MAS ATLAS 3 Analysis Complete	08/95
POAM H_2O Algorithm Complete	09/95
POAM Data Validation Complete	03/96
WVMS	
Deployment to New Zealand	01/94
Deployment to Mauna Loa	11/95
OOAM	
Flight Sensor Delivery	11/95
Launch	08/97
MAHRSI	

First Flight - Space Shuttle	10/94
Data set complete	03/95
Refurbish ICCD Camera	01/96
Deliver to KSC	01/97
CRISTA-SPAS II Flight	07/97
MAP Theory	
Models operational	09/94
Validation with WVMS	03/95
Validation with MAHRSI and MAS	05/95
CHEM2D for H_20, O_3 & CO_2 complete	09/95
Solar Forcing	
Assemble time series	06/95
Update line emission database	TBD
UVRS DBS	
GUI Version 1.0 complete	06/95
RAIDS upgrade to Version 1.0	TBD
ARGOS upgrade to Version 1.0	TBD
GIMI & HIRAAS Delivery	03/96
Launch of ARGOS	03/97
Final report and transfer of program	09/96
Lower Atmosphere	
Clear Sky Mission	04/94
Cloud heating/ARESE Mission	10/95
Conduct mid-latitude ozone mission	03/96
Cloud properties/satellite calibration mission (I)	05/96
Complete UAV payload integration and checkout	08/96
Final report and transfer of program to DOE	09/96

The above schedule includes activities beyond the termination of the ARSAP program. OOAM and ARGOS launches will occur in 1997 as part of the Space Test Program. Launch is supported through that program. Operations for the POAM and OOAM programs transitions to programmed and approved Navy RDT&E support through at least 1999. Delivery of the OOAM and ARGOS hardware will occur in early 1996 and is the final hardware activity to be supported by SERDP FY96 funds. Prelaunch support for these activities should be conducted during FY96.

10. Transition Plan:

Lower atmosphere measurement techniques will transition to DOE, with DOE paying operating costs when development is complete. In addition to this primary transition path, we will work with NOAA and DMSP to explore transitioning instruments to satellites. All data will be available through the DoD BDC at NRL and the GCDIS center at Oak Ridge. Middle and Upper atmosphere measurement techniques include: the semi-operational POAM sensor,

RAIDs and HIRAAs transition to DMSP, and converged weather satellite sensors. Ground-based sensors are commercially marketable meteorological instruments. Data from this and other activities can be used to provide climate data for long term atmospheric change.

11. Funding: $(K)

FY92	FY93	FY94	FY95	FY96	TOTAL
10,000	33,300	25,874	13,115	725	83,014

12. Performers:

Work will be conducted in-house at NRL, Sandia, Brookhaven, Argonne, Los Alamos, Pacific-Northwest, Lawrence Livermore National Labs. University participants include Penn State, Johns Hopkins, Wisconsin, North Carolina State, Harvard, Maryland, Colorado, Colorado State, California at San Diego, Oklahoma, and Alaska. ARM research is also underway with grants from DOE to scientists at NASA Centers and with cooperative arrangements with National Science Foundation and NCAR. Industry participants include Computational Physics Inc, General Atomics, Aurora Flight Services, Ross Aviation, Thermoelectron Technologies Corp., Research Support Instruments., Millitech Corp., ARTEP, SFA, University Space Research Associates, CNES, PRAXIS, SWALES, Federal Data Systems, Allied Signal, Falcon Research, Mission Research Corporation, and ATC.

International Agreements: DoD - Two experiments (POAM II & POAM III) to measure constituents of the polar stratosphere important to atmospheric photochemistry are conducted under contracts with the French National Space Agency (CNES). POAM II was launched on 25 September 1993 on the French SPOT 3 Earth Imaging Satellite. Design and engineering work are underway to launch POAM III on the SPOT 4 satellite in early 1997. Additionally, French scientists participate in the analysis of the POAM II data.

MAHRSI is part of an interagency, international collaboration, including NRL, NASA, USAF, and BMDO in the U. S. side and the German Space Agency (DARA) and University of Wuppertal in Germany. MAHRSI was launched in November 1994 on Space Shuttle mission STS-66, as part of the CRISTA-SPAS (Shuttle Pallet Satellite) mission. ASTRO-SPAS is a short-duration free flying spacecraft deployed and retrieved by the Space Shuttle. It was developed entirely by the German Aerospace Corporation (DASA) under contract to DARA.

Millimeter Atmospheric Sounder (MAS) project is an international collaboration consisting of NRL, several U.S. universities, Max-Plank Institute for Aeronomie in Germany and the University of Bern in Switzerland.

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14. Keywords:

Global Change, Ozone, Greenhouse, Atmospheric Remote Sensing, Global Warming, Radiation Budget

SERDP FY96 Project

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Acoustic Monitoring of Global Ocean Climate

3. **Agency:** Advanced Research Projects Agency (ARPA)

4. **Laboratory:** Scripps Institution of Oceanography

5. **Project ID:** #286

6. **Problem Statement:**

Conduct a "proof of concept" basic research program to measure, analyze, and determine the changes in global ocean temperature to advance our understanding of short and long-term ocean variability and its relation to climate trends. The oceans play a key, but still poorly understood, role in the most important processes contributing to climatic changes such as heat and carbon dioxide storage. The main goal of this proposed research is to measure directly global ocean temperature trends using innovative underwater acoustic technologies, based on the fact that the speed of sound in water is proportional to temperature. A further goal is to develop an ocean-atmosphere modeling capability and supporting database to permit skilled forecasts of significant global environmental changes, which are of major impact in global change and climate prediction. Issues are (1) resolving the complex acoustic signal structure in order to track long term trends along specific acoustic paths, and (2) extracting the long-term trends from the background natural variability of the oceanic temperature field. Methods will be developed to incorporate these measurements into climate prediction models, and to merge them with satellite temperature and altimetry data acquired in other research programs.

Background: Since ocean temperature is a key indicator of global climate change, accurate temperature measurements, spanning the world's ocean basins and sampled over a long period, are essential to complement atmospheric measurements of global climate trends. The capability to make synoptic temperature estimates derived directly from acoustic travel time measurements was demonstrated in the 1991 Heard Island Feasibility Test (HIFT) where acoustic signals were transmitted from a location in the Southern Indian Ocean to 14 receiver stations, manned by nine international scientific teams, in the Atlantic, Indian, and Pacific oceans. The test demonstrated that acoustic signals can be received over global paths with sufficient signal to noise ratios to measure propagation time and spatial variability.

7. **Project Description:**

Status: The Acoustic Monitoring of Global Ocean Climate program was approved by the SERDP Council and the Scientific Advisory Board (SAB) with the Congress providing initial funding in the Supplemental FY92 legislation. The SAB noted that; "This ambitious proof of concept experiment is a follow-on to the successful three-week long, 'Heard Island'

hypothesis testing experiment. Excellent scientists have been associated with this experiment and peer review protocols are used by its management. The ....broad international participation makes technical, economic, and political sense." ARPA competitively selected two university/industry teams for funding. This research effort will be complete in FY96.

Approach: Acoustic sources are to be placed on the ocean floor near the deep sound channel (800-1000 m) and periodically transmit encoded signals of 20-minute duration at 70 Hz. Deep sources direct maximum signal power into the long-range horizontal paths, providing good signal to noise ratios at long range. These sources will require state of the art manufacturing techniques to develop the specified 70 Hz acoustic devices. Both vertical and horizontal arrays will be used to resolve acoustic arrival structures. The program uses the Navy's Integrated Undersea Surveillance System receiver assets and deploys newly developed vertical line arrays (VLA) that are moored on the sea floor. Each VLA contains 40 hydrophones and advanced signal collection, timing, and processing modules.

In a complementary technology development, the Woods Hole consortium is developing a unique surface suspended, "drifting" acoustic receiver (SSAR). Through innovative use of satellite telemetry and global positioning system support, these drifting receivers will independently receive acoustic signals, fix their own position, process the received acoustic data; and then transmit all these data to a shore-based center via satellite link. Ten SSAR receivers will be built and deployed to complement the fixed receivers in locations that best utilize the SSAR's mobility features.

8. Expected Payoff:

The program will directly benefit the wold ocean research community in providing a unique ocean temperature data set which is expected to significantly improve short-term ocean forecast and warming products and provide reliable seasonal climate forecasts. These products are a key input to science-based governmental policy development on the effects of global warming.

The emerging science of acoustic thermometry will enable broad ocean climate variability research by the international oceanographic community, since the signal will be available to any country wishing to participate with their own acoustic receiver assets.

Development and application of coupled ocean/atmospheric modeling and prediction systems will lead to such practical applications as better prediction of "El Nino" effects throughout the Pacific with recommendations on minimizing the economic impact.

Advances in low frequency sources manufacturing technologies will provide the cost reduction, reliability and system performance needed for other long-term ocean data collection programs.

SSAR receiver offer promise of a low cost method for long-term studies of ocean climate variability, ocean geophysics, monitoring of natural and man-made seismic and environmental monitoring, e.g., pollution tracking.

The results of comprehensive marine mammal monitoring will provide benchmark scientific data never before available on the impacts of low frequency sound on marine mammal behavior, to aid in setting better, environmentally safe criteria for noise in the sea.

9. Milestones/Accomplishments:

The acoustic source, incorporating untried technology and design, has been successfully tested at sea and one source is presently deployed off the coast of California. The fixed network design, mechanical endurance testing of receivers, and the data handling/processing architecture have proceeded through all critical review and all stations are receiving the California source transmissions. Ocean climate models have been developed and validations are in progress with actual data. Marine mammal research associated with the California acoustic source is in progress. Only the state of Hawaii permits are needed to install/operate the Hawaii source. The milestones are as follows:

1.	Install Russian fixed receiver	10/95
2.	Install/operate California source	11/95
3.	Commence ATOC data collection	11/95
4.	Commence California MMRP Protocol	11/95
6.	Deploy SSAR receivers	02/96
7.	Install/operate Hawaii source	03/96
7.	Install Guam fixed receiver	03/96
8.	Complete six month MMRP protocol	04/96
9.	End acoustic transmissions	09/96
10.	Preliminary ATOC data analysis	09/96
11.	MMRP preliminary report	09/96
12.	Recover acoustic sources and VLA receivers	10/96

10. Transition Plan:

Funded entirely by SERDP, this basic research experiment in the Pacific Ocean is using state of the art ocean temperature detection technologies to detect climate change variability. The extension of these techniques to a long-term monitoring effort in the Pacific Ocean and perhaps subsequently globally will depend on the results of the Marine Mammal Research Program (MMRP) which is being accomplished concurrent with the acoustic data collection effort. A number of organizations have expressed a keen interest in continuing this research effort over a long term (10 year) period and they include NOAA, US Navy, and several international research organizations.

11. Funding: $(K)

FY92	FY93	FY94	FY95	FY96	TOTAL
7,000	2,4000	20,300	3,700	2,000	57,000

12. Performers:

Key scientists from the following research institutions and universities are collaborating in the program: Scripps Institution of Oceanography, Woods Hole Oceanographic Institution/Penn State University, Applied Physics Laboratory/University of Washington, University of California/Santa Cruz, Massachusetts Institute of Technology, Cornell University Laboratory of Ornithology, Hubbs-Sea World Research Institute, University of Michigan, Florida State University, Mississippi State University, University of Alaska, Naval Post Graduate School, Naval Research Laboratory/Stennis Space Center, NOAA Laboratories in Boulder and Miami, Research Planning Inc., Marine Acoustics Inc., Southern Methodist University/Mission Research Corp., Science Applications International Corporation, and University of Texas, Austin.

Active collaboration is scheduled with Australian, Canadian, French, German, Indian, Japanese, New Zealand, Russian, South African, and Taiwanese scientists.

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14. Keywords:

Global Warming, Acoustic Thermometry of Ocean Climate, ATOC

TABLE XVII FY 1996 POLLUTION PREVENTION	FUNDING $(K) FY96	ID Number	Page Number
Paint Stripping/Coatings			
Life Cycle Engineering and Design Program (EPA)	220	304	PP-4
Organic Protective Coatings and Application Technology (N)	303	65	PP-11
Fluorinated Ship-Hull Coatings for Non-Polluting Fouling Control (N)	606	756	PP-16
Aircraft Depainting Technology (N)	423	81	PP-23
High-Performance, Lead Free Electrical Sealants (DOE/AF/N)	230	429	PP-27
Solvent Substitution and Low VOC Cleaners (N)	121	67	PP-30
Laser Cleaning and Coatings Removal (AF)	15	139	PP-34
Large Area Powder Coatings (AF)	264	121	PP-38
Advanced Materials/Processes			
Rapid Testing for Acceptable Materials and Processes (AF)	144	117	PP-43
Other Hazardous Wastes			
Capacitive Deionization for Elimination of Wastes (DOE)	560	436	PP-47
Acid Recycle (DOE)	200	422	PP-54
Recycle Boiler Nitrite Solution (N)	200	69	PP-58
Use of Biomass Technologies on Military Installations	550	227	PP-61
Integrated Expert Solvent Substitution Database (EPA)	1,000	331	PP-65

TABLE XVII FY 1996 POLLUTION PREVENTION	FUNDING $(K) FY96	ID Number	Page Number
Point Source Emission Reduction			
Trapped Vortex Combuster for Jet Engines (AF)	500	1042	PP-71
Metal Working Process			
Alternate Electroplating Technology (N)	303	71	PP-77
Solid State Metal Cleaning (AF)	578	116	PP-81
Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys (A)	172	673	PP-84
Aircraft Maintenance Chromium Replacement (N)	193	66	PP-88
Non-Chemical Surface Preparation (AF)	641	130	PP-92
Recycling/Purification of Plating/Cleaning Baths (N/AF/EPA)	440	70	PP-96
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)	267	632	PP-101
Ordnance Materials and Processing			
Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion (A)	138	680	PP-107
Extraction & Recycling of LOVA Propellants Using Supercritical Fluids (A)	300	660	PP-114
Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computional Chemistry Models for Predicting Effective Solvents (A)	200	695	PP-118
Non Ozone Depleting Sealants for Ammunition Applications (A)	337	674	PP-123

TABLE XVII FY 1996 POLLUTION PREVENTION	FUNDING $(K) FY96	ID Number	Page Number
Solventless Manufacture of Propellants using Thermoplastic Elastomer Binder (N)	250	867	PP-127
DoD/DOE Clean Agile Manufacturing of Energetic Materials (N/DOE)	2,500	63	PP-130
Pollution Prevention Enhancement (TBD)*	3,000		PP-135
Solventless Pyrotechnic Manufacturing (N)	100	757	PP-136
Fire/Explosives Suppression			
Encapsulated Micron Aerosol Fire Suppression Technology (AF)	247	113	PP-142
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A/NIST)	248	682	PP-146
Chemistry of Halon Substitutes (A)	165	666	PP-151
Advanced Streaming Agent (AF)	400	158	PP-155
Refrigerants			
Non-Ozone Depleting Refrigerants for Navy Chillers (EPA)	410	309	PP-159
Pollution Prevention Total	16,225		

* Congressional Interest Item

SERDP FY96 PROJECT

1. SERDP Thrust Area: Pollution Prevention

2. Title: Life Cycle Engineering & Design Program

3. Agency: Environmental Protection Agency (EPA)

4. Laboratory: National Risk Management Research Laboratory (NRMRL)

5. Project ID: #304

6. Problem Statement:

During this decade, an increasing emphasis has been placed upon pollution prevention as a means to produce better products and systems while reducing environmental impacts from those systems. Several assessment tools and analytical techniques have been applied to environmental problems to improve system design and influence decision-making. However, most of these techniques, such as pollution prevention opportunity assessments, only look at on-site issues, ignoring impacts that might exist either upstream or downstream of the process. There may be cases wherein a cited pollution prevention alternative may in fact be more harmful. The problem for the Federal Government is that a decision to change a process for on-site benefits may produce adverse off-site impacts. Those impacts may in turn become regulated, or certain chemicals may become banned, stopping the alternative system and imposing lost capital costs.

Life Cycle Assessment (LCA) methodology is currently being applied to operations, systems, products and activities as a means to guide system design to ensure that alternative approaches are less burdensome. LCA differs from other pollution prevention techniques in that it views all the resource, energy and cost inputs to a product (Life Cycle Inventory), as well as the associated waste streams, health and ecological burdens (Impact Analysis), and evaluates opportunities to reduce environmental impacts (Improvement Analysis) from cradle to grave.

The LCA tool meets the SERDP RD&D goal to "address matters of concern to unencumber military operations, enhance military systems' effectiveness, and improve the safety of personnel in meeting the Department's environmental obligations." Only through the application of a cradle to grave analysis and engineering design approach in the development of military systems can the DoD be assured that a specific system is operating effectively with minimal environmental impacts. Because the projects selected involve technologies with broad applications in public and private sectors, this proposal also supports SERDP's goal to, "help solve significant national and international environmental problems through the application of the Department's technical capabilities, analytical systems and information."

LCA design emphasizes integration of environmental requirements into the earliest phases of the life cycle and successfully balancing those requirements with performance, cost, cultural and legal

criteria. LCA design will enable DoD to meet SERDP research and development objectives in (1) the development of non-hazardous alternate defense unique paints (e.g., CARC), (2) development of cost effective and non-polluting improved industrial processes and low VOC substitute chemicals for depainting and (3) the development of predictive methodologies to aid in the development of environmentally sound weapon systems throughout their life cycle and decommissioning.

7. Project Description:

The thrust of this program will be to take selected innovative technologies and products, applying life cycle design analyses to them to determine the net environmental and cost burdens. The LCA will apply methodology and design techniques previously developed under this Laboratory's programs. Since 1994, the Life Cycle Engineering and Design Program has developed the following projects:

1. MEK Substitute in Aircraft Radome Depainting

Under the EPA's WREAFS (Waste Reduction Evaluations at Federal Sites) program, NRMRL has researched and evaluated substitutes for methyl ethyl ketone (MEK) as cleaners and solvents in aircraft maintenance operations in the Oklahoma City ALC at Tinker AFB. OK-ALC performs maintenance, structural repair and refabrication of USAF aircraft, including the B-1B, B-52, KC-135, E-3 and other large aircraft. OK-ALC has reported MEK usage in excess of 5,300 gallons per year to wipe-down aircraft and over 8,200 gallons per year to depaint radomes.

From our research and in cooperation with Huntsman Chemical (formerly Texaco), NRMRL identified solvent formulations of propylene carbonate, n-methyl-pyrrolidone and dibasic esters as possible alternatives for MEK. These tests focused on the ability of the chemical mixtures to accomplish the job required and meet the same MILSPEC standard as MEK without major modification to operating procedures and equipment.

From this work, we have determined that a blend of 25% propylene carbonate, 50% n-methyl pyrrolidone and 25% dibasic ester (PC Blend) removed paint on test coupons in comparable time to MEK. Hardness tests showed that the PC Blend did not embrittle the fiberglass/epoxy substrate of the radome, nor did it effect flexural properties. Scanning via electron microscope indicated no significant damage to the fibers or fiber matrix interface. Test samples were repainted and demonstrated complete adhesion. For solvent properties, the PC Blend compares favorably with MEK. The PC Blend has a flashpoint of 210 F (against MEK's 20 F), low toxicity and lower evaporation rate.

The Life Cycle Engineering & Design Program evaluated this new formulation in an LCA approach that investigates the energy and environmental impacts of the product as well as the engineering design of the system in which it is used. Methodology laid down in NRMRL's manual, "Life Cycle Assessment: Inventory Guidelines and Principles," was applied. An inventory of the depainting operations was conducted to determine the resources necessary and actual environmental impacts of using the PC Blend. An Impact Assessment determined the

environmental consequences of depainting, including the production, use and disposal of the PC Blend product. The Improvement analysis evaluated the environmental consequences of the PC Blend, given OK-ALC's interest in using the product as a stop gap during an expected slow transition to a mechanical stripping system.

2. Improved Chemical Agent Resistant Coating (CARC) Applications

Another installation that has participated in assessments and evaluations under the WREAFS program, Ft. Eustis, completed a base-wide pollution prevention opportunity assessment the year before this project began. Under this assessment, a need for improvements in CARC painting and depainting operations was identified. Individual upgrades in on-site operations were made by changing over to alumina silicate, separating and recycling grit and acquiring HVLP painting equipment.

In cooperation with Ft. Eustis, an effort to study the Life Cycle impacts of vehicle painting with CARC is continuing under the WREAFS Program with SERDP sponsorship. Currently, DoD painting operations utilizing Chemical Agent Resistant Coatings (CARC) generate VOC emissions and hazardous waste. This program will identify environmental and energy burdens of CARC painting, identify and test potential improvements on a life cycle basis.

The LCA of CARC painting and depainting operations began with an inventory analysis to determine the resources used and environmental releases. An impact analysis was completed to determine all the environmental consequences associated with CARC operations, including corrosion control techniques. An improvement analysis was then conducted and it offered operational improvements that we are planning to test during the current year in a technology evaluation under this program.

3. Enhanced Methods for Life Cycle and Total Cost Assessments

As originally proposed, this part of the Life Cycle Engineering & Design Program sought to test and develop aspects of Total Cost Assessment (TCA) for the benefit and use of DoD and DOE operations and facilities. Like LCA, TCA incorporates the entire life cycle of a product or process, but TCA focuses on the internal and external costs that will be incurred. While LCA provides a range of information to support environmental decision-making, cost information is not typically integrated with LCA environmental release data. Integration of cost data into the LCA approach will enhance its utility as a decision support tool. Under the original proposal, a weapon component called the Gas Transfer System was proposed to test the integration of these methodologies. However, the project team decided early that there was a greater opportunity in focusing on the GBU-24 instead, and developing measurement protocols under DOE's alternative feedstocks program.

In cooperation with Picatinny Arsenal, Office of Naval Research and Los Alamos National Laboratory, this project applies LCA engineering and design principles to the design and development of weapon systems and energetics, identifying existing or potential environmental

problems that may be caused anywhere within the product system, from well head to final disposal. The product for this evaluation is the GBU-24 bomb.

For weapon system design and development, we are cooperating with Picatinny Arsenal to demonstrate the incorporation of LCA methodology into the GBU-24 and develop information as a model for future use leading to the widespread application to other design agencies. Currently, a full LCI is underway, with an impact analysis planned for FY96. A significant feature is the comparison of the current energetic, RDX, which has to be milled to shape, with TNAZ, a new energetic that can be molded to shape, re-melted and re-used.

Under a cooperative agreement with Battelle Memorial Institute, LCI data has been collected and analyzed for RDX, and Los Alamos is contributing data on the new energetic, TNAZ, for an LCA comparison. This project is related to the larger SERDP research effort being conducted by Picatinny.

8. Expected Payoff:

The overriding benefit from all projects would be the testing and customizing of LCA design and TCA approaches for DoD applications, as each project provides lessons learned in using these tools. From each project, these payoffs are expected:

MEK Substitute in Aircraft Radome Depainting

The anticipated benefits include the elimination of a 33/50 (EPA 17) toxic chemical from the radome depainting operation, along with the VOC air emissions. Our evaluation of the PC Blend demonstrated an annual savings of over $30,000 from using the PC Blend instead of MEK in radome operations alone. OK-ALC is currently testing mechanical technologies for paint stripping, but has not yet experienced success with radomes. They have indicated the desire for the PC Blend to act as a transitional alternative, provided it meets all performance criteria.

Improved CARC Applications

While CARC material is undergoing tests and reformulation to reduce VOC content, this project is expected to generate guidance with applicability to facility CARC painting operations throughout the Army and DoD-wide. Techniques and product improvements will be implemented to ensure that more paint meets the truck, generating cost savings and increasing operational efficiency. Lessons learned here will have application to all DoD CARC operations in Army, Air Force and Navy/Marine facilities. EPA's WREAFS program will provide additional support in evaluating the potential for application of lessons learned to marine anti-fouling paints and coatings.

Enhanced Methods for Life Cycle and Total Cost Assessments

In this project, we have the opportunity to avoid environmental problems as the next generation of a weapon system is being designed. This is particularly important when the weapon has been designed for a specific use, but has outlived its usefulness and is not easily disposed of for regulatory reasons. There are significant differences in the ease of demil for a bomb equipped with RDX as opposed to TNAZ. Some of these differences will be demonstrated with clarity through the application of TCA, enabled better informed planning for DoD.

9. Milestones/Accomplishments:

1. Program Start 12/94

Planned start date was delayed four months due to late arrival of seed funding. Initial work was begun on program planning and literature searches in-house.

2. Develop LCA Approach & Research Plan 01/95

Completed on schedule thanks to in-house support from NRMRL (RREL). The decision to reorganize the DOE segment of this work to focus on energetics and the GBU-24 was made. Work assignments were issued along with a cooperative agreement (Battelle) to initiate the LCAs of PC Blend, CARC and the GBU weapon system.

3. Define Life Cycle of Project Operations & Refine Plan 02/95

Found to be unnecessary, thanks to the in-house support and the cooperation of our partners in providing on-site support.

4. Complete LCA/LCD Inventories & Impact Assessments 01/96

The LCA inventories and impact assessments were completed three months ahead of schedule (11/95) and the reports are currently undergoing EPA/DoD review for clearance to publish. The PC Blend report, entitled, "Life Cycle Assessment of an Alternative Chemical Depainter in ALC Operations" has been reviewed and should be cleared in time for publication this quarter. Also, this past year, OK-ALC procured sufficient PC Blend to depaint full-size radomes, rather than just the test coupons of the previous tests. The results of the tests on the two radomes showed a PC Blend depainting performance equivalent to MEK. In regards to the CARC report entitled, "Life Cycle Assessment of Chemical Agent Resistant Coatings in Painting and Depainting Operations," it is currently under review and should be cleared in time for publication this spring. The report on the GBU 24 did not have sufficient data to qualify a comparison between energetic materials and that data is currently being generated by Los Alamos for us. In addition to these reports, we generated two additional reports in draft entitled, "Industry Study: Alternative Coating Removal Methods for Military Operations," and "Air Quality Regulatory Impacts on Military Cleaning and Coating Operations" which were judged necessary to provide wider view of operations and impacts.

5. Report Findings 02/96

This effort is intended to be a review of our findings to date in order to be able to guide design efforts and technology evaluations in the improvements phase of this work. We are currently suffering under a serious scheduling set back caused by the recent furlough. In addition to being sent home, all outside work efforts were ordered stopped, causing an almost six week interruption. However, we are proceeding to set up a technology evaluation for CARC on the basis of lessons learned, and hope to be able to initiate it this month.

6. Identify Alternative Materials and Engineering Designs 03/96

Underway.

7. Select Technologies/Products for Evaluation 04/96

CARC is currently being developed, others should meet this schedule.

8. Report Evaluation. LCA Design Report. 12/96

The LCA Design Report will bring together lessons learned from all the projects. It will also include references from other LCA program research (such as automotive, photovoltaic, etc.) Where lessons in the applications of methodology are relevant to DoD operations.

10. Transition Plan:

Technology and information is being transferred through a number of vehicles. We have been working through industry contacts and panels, electronic bulletin boards such as PPIC/Enviroene, the National Technical Information Service (NTIS) and other Federal mailing lists and networks as planned. The CARC work has broadened to include most of the Army installations conducting painting operations. We are cooperating with the Air Force Institute of Technology (AFIT) in providing lectures at environmental courses at WPAFB and we are sharing information with the Air Force Center for Environmental Excellence at Brooks AFB. A series of presentations and papers on this work have been presented at national meetings such as the AWMA national meeting, the Air Force Worldwide Pollution Prevention Conference and other scientific research meetings.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	750	180	220	300	300	1,750
EPA	200	200	200	200		800
TOTAL	950	600	500	500	300	2,550

12. Performers:

Tinker AFB, OK-ALC, with Thomas Walker as the point of contact, and Huntsman Chemical (formerly Texaco) in the PC Blend Study. Ft Eustis Army Transportation Command, with Helen Worthington as the point of contact, are supporting the CARC work, along with other Army installations providing data. For our work in energetics, we are cooperating with Picatinny Arsenal, with Larry Laibson as the POC and the Office of Naval Research (Jim Short) and Los Alamos National Laboratory (Ker Chi Chang).

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14. Keywords:

MEK, Painting, Depainting, Solvents, Computer Modeling, LCA

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Organic Protective Coatings and Application Technology

3. **Agency:** U.S.Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX)

5. **Project ID:** #65

6. **Problem Statement:**

To develop high performance, non-toxic, low volatile organic compounds (VOC) content coatings for Navy use. Organic coatings are the primary source of protection against environmental degradation for Navy aircraft (A/C), weapon systems (WS) and support equipment (SE). In addition, these materials provide passive countermeasures against many enemy threats. There are a large number of different coating systems currently used by the Navy due to the diverse nature of their functions; the variety of substrates & alloys to which they are applied; and the severe nature of their operational environment. These protective coatings contain toxic inhibitors (i.e. lead, chromates, etc.) and high VOC contents. These components are released during painting operations as organic and toxic air emissions. Federal, state and local environmental agencies like the EPA and California Air Quality Management Districts (AQMD) classify these materials as hazardous and restrict their emissions through regulations such as the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act (RCRA) as well as local EPA and AQMD rules. In addition, CNO directives require significant reductions in the amount of hazardous waste generated by the Navy. Finally, painting operations at maintenance depots are a major contributor to hazardous material and waste generation in the DOD. Therefore, it is necessary to develop new high performance coatings that meet current and future environmental restrictions while allowing the Navy to continue painting operations. This effort is covered under the Tri-Service Environmental Quality Strategic Plan; Pillar 3: Pollution Prevention, Requirement Thrust: 3.1.4.h: Non-Hazardous Aircraft Paints and Coatings and is a continuation of an existing 6.2/6.3 effort.

7. **Project Description:**

A full spectrum approach for reducing the VOC and air toxic emissions from protective coatings is being pursued. To begin with, investigation in low VOC polymer technology has been used to produce low VOC binder systems. Reactive monomers and diluents have been developed to obtain low viscosity, low VOC binder systems for future organic coatings. In addition, recent advances in water-borne resin technology has allowed for the development of a high performance water-borne topcoat which goes beyond mere compliance with environmental regulations. Coating corrosion resistance, physical performance properties and VOC content were evaluated in the development of the best materials. Furthermore, low/no VOC protective coatings (such

as electro-coatings, powder coatings, 100% solids coatings, 100% water-based coatings, etc.) are also being researched for potential aerospace applications. Several recently developed VOC compliant, non-toxic alternative materials have been investigated for this program. These compliant coating systems include compliant lacquer topcoats and non-toxic inhibitor systems. The non-toxic inhibitor systems were used to formulate replacements for the current lead and chromate containing materials. These new materials will be optimized, service evaluated and implemented for Navy use. Finally, conventional air spray equipment used to apply these materials, has a transfer efficiency of only about 28%. Therefore, implementing high transfer efficient spray equipment would significantly reduce the amount of air emissions from painting operations. Application equipment such as air-assisted airless, electrostatic, and high volume low pressure (HVLP) wave been evaluated and HVLP spray guns are being implemented in naval aviation facilities.

8. Expected Payoff:

The development of non-toxic, VOC compliant coatings will enable the Navy to meet current and future environmental regulations as well as reduce the total amount of hazardous waste the Navy generates. In addition, these new materials will eliminate the need for the installation of extremely expensive control equipment (i.e. $1-5M per spray booth for VOC emission control). Finally, the implementation of high transfer efficient spray application equipment is required under the Clean Air Act. This effort is in direct support of Navy and DOD hazardous waste minimization policies/directives. In addition to reduced handling and disposal costs, Navy A/C and equipment operational readiness will be maintained by using these new coatings. This is particularly important considering the cost of these A/C, WS, and SE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to the commercial sector (aerospace, automotive, marine, etc.).

9. Milestones/Accomplishments:

1. Characterize Non-Toxic Inhibitors for Organic Coatings	09/92
2. Develop/Optimize Compliant Lacquer Topcoats	09/92
3. Service Demonstration of Compliant Lacquer Topcoats	09/93
4. Develop Water-Borne Topcoats	09/93
5. Develop Non-Toxic Inhibited Organic Coatings	12/93
6. Evaluate High Transfer Efficiency Application Equipment	12/93
7. Initiate Low VOC Polymers investigation for A/C Coatings	12/93
8. Optimize Water-Borne Topcoats	06/94
9. Complete Compliant Lacquer Topcoats demo	06/94
10. Optimize Non-Toxic Inhibited Primer Coatings	09/94
11. Implement High Transfer Efficiency Application Equipment	09/94
12. Develop Epoxy A/C Topcoats Based on Low VOC Polymers	09/94
13. Initiate Non-Chromate A/C Sealant Investigation	10/94
14. Initiate Water-Borne Topcoat Service Demo	11/94
15. Implement Compliant Lacquer Topcoats (Spec revision)	06/95
16. Initiate Non-Toxic Inhibited Primer Demo	10/95

17.	Evaluate Low/No VOC Polyurethane Resins for A/C Coatings	10/95
18.	Develop Powder Coatings for A/C Applications	12/95
19.	Develop Electrocoatings for A/C Applications	12/95
20.	Full Scale Demo of Optimum Water-Borne Topcoats	01/96
21.	Develop Non-Chromate A/C Sealant	04/96
22.	Transition Low VOC Urethanes for A/C Coating Development	06/96
23.	Implement Non-Toxic Inhibited Organic Coatings	07/96
24.	Initiate Powder Coatings for A/C Applications	09/96
25.	Initiate Electrocoatings for A/C Applications	09/96
26.	Optimize Non-Chromate A/C Sealant	10/96
27.	Implement Water-Borne Topcoats (Spec Revision)	10/96
28.	Service Demonstration of Non-Cr Sealants	06/97
29.	Complete Service Demo of Powder Coatings	09/97
30.	Complete Service Demo of Electrocoatings	09/97
31.	Implement Powder Coatings	09/98
32.	Implement Electrocoatings	09/98
33.	Implement Non-Chromate Sealants	09/98

Material problems which arose from the water-borne topcoat demonstration have been resolved through a cooperative Navy/industry effort and another technology demonstration is scheduled for January 1996. Also, a service demo was performed on a P-3 aircraft, "beaver tail", panel in Feb 95. A low VOC epoxy aircraft topcoat formulation has been developed based on reactive diluents. A patent disclosure has been submitted on the non-toxic inhibited primer. Novel polyurethane resin systems are being investigated for the low VOC polymer technology effort for future A/C coating development. A service demo of the non-chrome primer was performed at NADEP Jacksonville in the fall of 1995. A new Navy report entitled "High Performance, Low Volatile Organic Compound (VOC) Content Epoxy Systems for Naval Aircraft Coatings", has been prepared and is pending publication. Lab evaluation of low/no VOC polyurethane resin systems and coatings was initiated. A field demo of a production batch of the two-component water-borne topcoat was conducted at NADEP Jax on a large test sheet. A full scale demonstration is expected in March 1996.

An investigation of MC-521 Morton International inhibited, non-chromated polysulfide sealant was started. This material has the potential to meet all mechanical and corrosion properties for spraying surfaces and fuel tank sealants. A revision to MIL-S-81733 (the chromated sealant spec) to a production specification is planned in FY 96 to allow for inhibited, non-chromated materials. The 509 manual was updated to include new specifications and procedures. Military and industry personnel met via the Joint Group for Aerospace Pollution Prevention (JGAPP) Team for analysis and demonstration of non-Cr primers.

MIL-P-23377 Addition of Non-Chromate Primer Class (N) To meet proposed Clean Air Act Rule. Demonstration of this technology is in progress & will continue in FY-96. Spec was also revised to eliminate all Non-VOC compliant classes and all ODS chemicals.

MIL-P-85582 Addition of Non-Chromate Primer Class (N) To meet proposed Clean Air Act Rule. Tech Demo on-going. One Material Qualified to the Non-Chromate class. Spec was also revised to eliminate all non-VOC compliant classes and all ODS chemicals.

MIL-C-81352 Addition of a Water-Borne Polyurethane Class (II) to provide a low VOC one-component touch-up coating to meet proposed Clean Air Act CTG Limits. Service demonstration of 2 materials in progress.

TT-P-2760 Addition of Non-Chromate Primer Class (N) to meet proposed Clean Air Act Rule.

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at Naval Aviation Depots through the Lead Maintenance Technology Center for Environment. Following demonstration, they will be transitioned to fleet use through specification modification, technical manual revision and design changes. NAWCADPAX has technical responsibility over the applicable military specifications and technical manuals requiring modification or revision. Industry coordination through out the development and evaluation of these materials and processes will insure availability for implementation.

11. Funding: $(K)

FY94	FY95	FY96	FY97	FY98	TOTAL
400	248	303	600	330	1,881

12. Performers:

Development of non-toxic, low VOC protective coatings is being performed/directed by the Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX) in conjunction with the Naval Air Systems Team. This Team consists of the Naval Air Systems Command, NAWCADPAX, the Naval Aviation Depots (North Island, Cherry Point, and Jacksonville) and the Lead Maintenance Technology Center for Environment. Headquarters, laboratory and field personnel are all supporting this project. In addition, this effort is being coordinated with resin/coatings industry (Miles Inc., Air Products, Deft, BASF, Spraylat, Courtaulds, etc.), Air Force (Tinker AFB, Kelly AFB and Tyndall AFB), Army Research Lab, aerospace industry (MDA, Boeing, etc.), equipment manufacturers (Graco, Binks, etc.), and technical societies (Aerospace Chromium Elimination Team).

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14. Keywords:

Organic Coatings, Materials Substitution, Paint Application Equipment, Low VOC Polymers, Volatile Organic Compounds, Non Chrome/Lead Coatings

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Fluorinated Ship-Hull Coatings for Non-Polluting Fouling Control

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Command, Control and Ocean Surveillance Center (NCCOSC), and Naval Research Laboratory (NRL)

5. **Project ID:** #756

6. **Problem Statement:**

The goal of this project is to develop non-polluting fouling resistant or fouling release hull coatings exploiting the low surface energy of surface oriented perfluorinated alkyl compounds. This project is a continuation of the FY93 funded "Innovative Very Low VOC Antifouling Paints and Processes" SERDP (6.2) program, and includes a new initiative in cooperation with NRL to explore the fouling release properties of low-glass-transition-temperature polyurethanes that have liquid-like surfaces. This project meets SERDP Pollution Prevention Objective 3 and associated with RELIANCE thrust area 3.b (Coatings and Treatment). It addresses the specific Navy requirements 3.I.8.h (Prevention of hazardous discharge from ship in-water hull cleaning).

Protection of ship-hulls from marine fouling organisms is essential for efficient fleet operation and energy conservation. To achieve this protection, ship hulls have been coated with antifouling paints that contain toxic material such as cooper or organotin. Conventional antifouling coatings create an environmental hazard due to continuous release of toxic materials. A cruiser size ship (35,000 ft^2 hull area) releases approximately 2 lb cooper/day that may bring approximately 5 million gallons of sea water to toxic copper concentrations. Dozens of ships painted with conventional toxic antifouling paints can make a significant environmental impact in an enclosed harbor.

Since the Navy operates both in US and foreign waters, compliance with Federal, State, local environmental regulations as well as with regulations imposed by the host countries is required to ensure unconstrained operation. To meet its needs, the Navy has a strong commitment to develop and maintain an environmentally sound ship for the 21st century. The present proposal is a contribution to this effort with the goal of developing a toxic free coating that resists or reduces the attachment of marine fouling organisms. This proposal takes advantage of the weak adhesion characteristics of materials that have low surface free energies.

All marine fouling organisms use biopolymeric adhesive secretions for attachment. The strength of adhesion, expressed as the work of adhesion (the work required to separate the adhered liquid form the solid surface) (W_A) and the liquid (Y_l) minus the interfacial tension (Y_{sl}) ($W_A = Y_s + Y_l -$

Y_{sl}, Dupre 1869). From this equation, it is clear that the lower the surface free energy of the solid (Y_s), the weaker the adhesion. Hull coatings with sufficiently low surface energy should prevent fouling because organisms would not be able to adhere to it.

The lowest surface free energies can be created by adsorbed monolayers of closely packed perfluorinated compounds. Since adsorbed monolayers are not practical as hull coatings, we propose to simulate them by grafting perfluoroalkyl compounds to surfaces, by embedding such molecules into the surface of polymeric matrices, and by binding the perfluorinated compounds into a polymeric backbone to create comb type polymers with perfluoroalkyl sidechains.

These types of polymeric materials have far lower surface free energies than Teflon and have promising properties for controlling biofouling. The key parameter is the molecular orientation at and immediately under the surface. Therefore, a major part of the proposed work will be dedicated to the elucidation of the molecular orientation of the various experimental systems. This knowledge will assist efforts in optimizing the orientation for minimum surface free energy and maximum performance as well as assessing the stability of the orientation in a seawater environment and the changes caused by the marine environment.

7. Project Description:

The specific objective of this project is to develop a nontoxic, zero discharge coating that protects ship-hulls from marine fouling organisms. Unlike conventional antifouling paints, such coatings will not contain toxic materials, rather they will be designed to resist fouling or allow only weak adhesion of fouling organisms. In order to minimize adhesion we will design materials with the lowest possible surface free energy. Our technical objectives are to: (1) Simulate adsorbed fluorinated monolayers either by grafting perfluoroalkyl molecules to surfaces, by embedding perfluoroalkyl compounds into the surface of polymeric matrices, or by synthesizing comb type polymers with perfluorinated side-chains for maximum effectiveness; (2) Determine the minimum amount of perfluorinated additive needed for optimum performance; (3) Reduce the amount of the expensive perfluorinated moiety by copolymerization of block-polymerization with non-fluorinated monomers to reduce cost; (4) Verify the effectiveness of the perfluorinated polymeric materials against the adhesion of marine fouling organisms.

Elucidation, control and stabilization of the surface orientation of the molecules and polymeric side-chains is a key technical issue. We will systematically optimize the curing and polymerization conditions to achieve consistent low surface free energies and antifouling/fouling-release properties. Additives and copolymerization are also important issues affecting surface property optimization and coat reduction. In addition to the surface free energy related measurements, the shear strength of a selected series of adhesives, including the mussel adhesive, will be determined. The adhesion strength will indicate the fouling release property of a polymeric surface.

Molecular modeling will help to verify and explain molecular orientations and interactions observed at the polymeric surface. We will use powerful computational chemistry programs such as Gaussian 92, SPARTAN and HyperChem on our Conter's Convex C3240 MiniSupercomputer.

We will use computational chemistry to calculate surface free energies of model compounds, design low adhesion surfaces, and predict surface effects and molecular interactions at various interfaces.

Long-chain perfluorinated compounds will be prepared from a number of derivatives of perfluoroalkyl iodide homologues. These include acrylates and methacrylates for use as additives or for polymerization to form comb-polymers. Olefins prepared from the iodides will be hydrosilylated to form perfluoroalkylethyl silanes. The silanes are used to form self-assembled chemisorbed monolayers and polysiloxane comb-polymers. The iodides are also used to form perfluoroalkylethyl thiols which are grafted to metal surfaces, such as geld, to also form chemisorbed monolayers. Adsorbed and chemisorbed molecular layers of perfluoroalkyl compounds with various functional groups will serve as model surfaces to study molecular orientation and surface characteristics.

Various techniques will be used to determine the surface configurations of the fluorinated moieties. These techniques include grazing-angle infrared reflectance to calculate molecular orientation, X-ray Photoelectron Spectroscopy (XPS) to determine CF_2/CF_3 ratios on the surface, and visible light and infrared ellipsometry to measure film thicknesses. The molecular depth profile of the surface layer will be determined by variable angle Attenuated Total Reflectance methods. Depth-profiling provides information about the concentration distribution of perfluoroalkyl additives near the surface and also about the conformation of the polymer molecules and orientation of the side-chains at the surface and in the underlying layers.

We will simulate adsorbed molecular layers by mixing perfluorinated amphipathic compounds into uncured polymeric mixtures. The compounds chosen as additives include perfluoroalkyl acids, alcohols, amines, and esters. The additives migrate to the surface and the hydrophobic portion of the chains extrude from the matrix so that they are immobilized oriented at the polymer surface. The advantage of using additives is simple preparation that requires only small quantities of the expensive perfluoroalkyl compounds to achieve sufficiently low surface energies.

Comb-polymers will be synthesized from monomers with long perfluoroalkyl chains or by grafting perfluoroalkyl chains to existing polymeric backbones. These simulate adsorbed monolayers, producing surfaces with surface energies comparable to those of adsorbed molecular layers. In addition to the presently explored polymer system, the acrylates/methacrylates and the siloxanes, we will synthesize several new classes of polymers such as urethanes, epoxies and polyethylenes containing long perfluorinated side-chains. We will systematically determine the optimum factors that control the orientation of the perfluorinated moieties at the surface.

Parallel with this effort, basic research (6.1) on fluorinated poly-urethanes with low glass transition temperatures will be initiated at Naval Research Laboratory. The potential advantages of these polymers (1) Low surface energies; (2) Low glass transition temperatures and high elasticity that may inhibit firm attachment of organism; (3) Low release energies that facilitates dislodging of the adherents; (4) Thermoplastic nature that simplifies waste disposal.

A recent development in oxetane chemistry has led to the synthesis of a new family of polyether glycols with fluorinated side-chains. Urethanes based on these new macromers have been successfully prepared at NRL. Results from preliminary tests showed that these urethanes resist attachment of barnacles and preserve the surface properties after a long period of immersion in water.

The goals of the 6.1 part of research are: (1) Incorporate longer fluorinated side-chains into the polymers to reduce the surface energy; (2) Optimize composition and synthesis; (3) Understand the interactions between water and surface during long periods of contact and the relation to release energy.

A new family of fluorinated polyether glycols will be prepared by oxetane chemistry. Fluoroalkoxymehyl-3-methyl-oxetane (FOX) is obtained by reacting 3-bromomethyl-3-methyl-oxetane with fluorinated alkoxides in DMF at 70°C. Ring opening polymerization of FOX monomers is then conducted at 18°C using a lewis acid catalyst. The structure and length of the fluorinated branch can be varied for optimum performance. The fluorinated polyether glycol is reacted with diisocyanates and diols to form polyurethane. By varying the composition, the properties of polymer will be optimized.

The physical properties of the polymers, co-polymers and mixtures prepared both at NCCOSC/RDTE DIV and at NRL will be characterized and optimized for durability and low surface free energy. Low surface energy has been used as the primary design criterion for materials for fouling release. Recent work at NRL with dynamic contact angle analyzer (DCA) provides additional information for characterization. To keep a surface clean, low release energy is required to release the new adherents. A measurement of this release energy is the receding contact angle.

Nanoscale chemical composition and mechanical properties of polymeric materials can vary significantly either laterally or vertically. These variations can be characterized with X-ray photo-electron spectroscopy (XPS) and atomic force microscopy (AFM). It has been shown at NRL that nanoscale mechanical properties may be quantitatively measured as a function of penetration depth using AFM as a nanoindentor. By obtaining a series of indentations and using a raster scan pattern across a surface, nanoscale three-dimensional mechanical property mapping may be performed on the sample surface. A recently developed algorithm which de-convolute results from XPS measurements can be used to perform corresponding chemical composition mapping. Structure-properties correlations in the surface region can be established.

The experimental coatings will be exposed to the marine environment to determine fouling resistance, fouling release, durability, and possible surface molecular changes caused by sea-water, biofilm and fouling organisms.

8. Expected Payoff:

Non-polluting, not-toxic antifouling coatings will be synthesized. This new antifoulant will have non-wetting low-energy surface which resists the attachment of the organisms. The low surface

energy antifoulant releases no toxic material into the environment; therefore, no environmental hazard will be created. While toxic antifoulants are specific against certain types of fouling, the low energy surfaces prevent any kind of attachment and provide universal protection. More importantly, in the low surface energy coating; since its efficiency is based upon a physical surface phenomenon and not on depletive active substance, long effective lifetime is ensured. Both the Navy fleet and commercial shipping industry are potential users of the non-polluting fouling release coating.

9. Milestones/Accomplishments:

1. Synthesis of perfluoro compounds, including polyfluorooxetanes manual method	03/94
2. Automate polymerization process	07/94
3. Automate polymer application process	08/94
4. Field exposure testing (1st formulation run)	09/94
5. Surface characterization studies (1st & 2nd rounds)	10/94
6. Synthesize 2nd round of polymers	01/95
7. Synthesize siloxane networks & block copolymers (NRL)	01/95
8. Evaluate surface dynamics in water of silicone networks (NRL)	01/95
9. Synthesize fluoroorgano-oxetane Networks (NRL)	06/95
10. Synthesize side-loop architecture polymers (NRL)	06/95
11. Characterize oxetane vs. siloxane vs. side-loop vs. block surface properties of best polymers	07/95
12. Optimize surface properties of best silicon network candidate (NRL)	09/95
13. Begin field exposure tests (NRL)	09/95
14. Complete three or more polymerization optimization cycles for acrylate systems (includes synthesis, characterization performance testing) (assessment of status)	09/95
15. Complete three or more polymerization optimization cycles (NRaD) (2nd round) (progress status assessment)	01/96
16. Optimize surface properties of best oxetane polymer candidates (NRL)	04/96
17. Complete two polymerization optimization cycles (NRaD) (3rd round) (progress status assessment)	05/96
18. Scale-up of synthesis of optimized oxetane candidates (NRL)	06/96
19. Field exposure testing (improved compositions) (NRL)	09/96
20. Optimize surface properties of best acrylate polymers (NRaD)	07/96
21. Prepare prime polymer candidates for long-term exposure study (NRaD)	08/96
22. Complete three or more polymerization optimization cycles (NRaD) (4th round)	09/96
23. Begin long-term exposure study with prime polymer candidates (NRaD/NRL)	09/96
24. Begin long-term exposure study with prime polymer candidates (NRaD/NRL)	11/96
25. Complete three or more polymerization optimization cycles (NRaD) (4th round)	12/96
26. Optimize surface properties of best overall polymer (NRL)	01/97
27. Scale-up of synthesis of best candidates (NRL)	04/97
28. Field exposure testing (latest batch) (NRL)	06/97
29. Correlate long-term field exposure data with predictors from surface	

characterization (NRaD/NRL) 07/97
30. Scale-up synthesis of optimized candidates (NRaD) 09/97
31. Optimize large scale coating application parameters (NRaD) 09/97

Low-surface energy easy-release coatings have been prepared. It has been found that the low-surface energy, although a major factor, is not the only determining factor in developing easy-release coatings. Other properties such as surface morphology, coating flexibility and thickness are important. We are pursuing optimization of such coating properties and are attempting to correlate their contributions to easy-release performance.

10. Transition Plan:

After successful demonstration, the low-surface-energy non-polluting fouling-release coating will be transferred to suitable private companies (e.g. GenCore Polymer Division) as defense conversion for commercial scale production, and the fleet (NAVSEA) for implementation. Through the NAVSEA/NSWC Advanced Technology Demonstration program on Non-polluting/biodegradable Antifouling Hull Coatings there is a high degree of coordination between performer and user.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	570	895	414	606	830	3315
NAVY	0	75	75	75	0	225
TOTAL	570	970	489	681	830	3,640

12. Performers:

The 6.2 portion of the project will be performed at NCCOSC/RDT&E Division Code 521, the 6.1 portion at NRL. The expertise of fluorochemical companies such as DuPont, 3M and GenCore Aerojet (Dr. Aslam Malik) will be recruited for synthesizing the necessary compounds and polymers. The development of the final coating will be performed with the cooperation of the paint companies (GenCore Polymer Division). Professor Joseph A. Gardella, Jr. of SUNY, Buffalo will be in charge of the XPS measurements. This project is coordinated with the ONR 6.1/6.2 Bimolecular Antifouling Program that includes developing and evaluating fouling release materials from industry, NRL and academic research. Also it will be coordinated with NAVSEA/NSWC Advanced Technology Demonstration program on Non-polluting/Biodegradable Antifouling Hull Coatings that started in FY93 and will test and evaluate fouling release and biodegradable natural antifoulant coatings.

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14. Keywords:

Antifouling Paints, Coatings, Low Surface Energy, Non-Polluting, Perfluoroalkyl, Fluorinated Polyurethane, Oxetane, Minimally Adhesive Surfaces, Release Energy, Receding Contact Angle, Nanoscale Surface Mapping

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Aircraft Depainting Technology

3. **Agency:** U.S.Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX)

5. **Project ID:** #81

6. **Problem Statement:**

To develop a non-hazardous replacement for chemical paint stripping used on Navy aircraft (A/C), weapon systems (WS) and support equipment (SE). Current chemical paint strippers contain hazardous components like phenols, methylene chloride and chromates. Paint removal operations at maintenance depots has been determined to be a major contributor to hazardous waste generation in the DOD. Federal agencies like the EPA and state agencies like the California Air Quality Management Districts (AQMD) have begun to restrict the use of these hazardous materials. Regulations like the Clean Air and Water Acts, RCRA and local EPA and AQMD rules limit or prohibit the use and disposal of these hazardous materials. In addition, CNO directives require significant reductions in the hazardous waste generated by the Navy. Several generic alternative stripping methods to the present chemical removers are being developed. These techniques need to be optimized and evaluated for use at Naval Aviation Depots. Therefore, to comply with existing and future regulations while maintaining aircraft performance and operational readiness, these alternative methods need to be investigated. This effort is covered under the Tri-Service Environmental Quality Strategic Plan: Pillar 3 - Pollution Prevention, Requirement Thrust: 3.1.5.a Non-Hazardous Paint Removal and is a continuation of an existing 6.2/6.3 effort.

7. **Project Description:**

Alternative methods of coating removal that meet increasing waste disposal constraints, have to be developed to maintain aircraft rework operations while reducing hazardous waste generation. Because there are so many different substrates/alloys and coating systems currently used by the Navy, these non-hazardous paint removal processes will also have to be versatile. Naval aircraft have different load bearing structures (higher strength) to withstand aircraft carrier landings. In addition, the Navy's operational environment can have a seriously deleterious effect on the structural integrity of aircraft skins. These issues complicate the stripping process for naval aircraft. This program will identify the best alternatives from existing and developmental methods such as non-hazardous chemical paint strippers (i.e. materials that do not contain chromates, methylene chloride, phenol, etc.), mechanical removal procedures (PMB, water jet stripping, etc.) and thermal removal methods (laser, FlashjetTM). Procedure efficiency, effects on substrate surface, hazardous waste generation and applicability will be investigated in order

to determine the best procedure for Navy applications. Comparison of techniques as well as advantages and disadvantages will also be performed. Mechanical removal procedures eliminate the use of hazardous chemicals, however, several individual mechanical techniques damage the substrate surface during the removal process. Since some sections of aircraft skins are very thin, this is not acceptable. However, if several techniques are combined to remove the coating the surface damage could be eliminated/minimized to an acceptable level. For example, one possible combination is flash lamp/dry ice stripping (Flashjet). The flash lamp degrades the coating system and the dry ice simultaneously removes the residue at a reduced pressure (i.e. reduced surface damage). The practical application of flashlamp/dry ice or waterjet will require the use of robotic assisted manipulation. Two manipulators are under investigation. The first is a mobile (vehicle integrated) semi-robotic system for depainting large aircraft. The second is a fixed gantry robotic system ideal for small aircraft and off-aircraft components.

8. Expected Payoff

The elimination of the majority of chemical paint strippers would significantly reduce the total amount of hazardous materials generated by the Navy. FlashJetTM stripping will reduce hazardous waste by 95%. Furthermore, requirements for emission control equipment for methylene chloride (estimated at $1M/facility) would be eliminated. This effort is in direct support of Navy and DOD hazardous waste minimization policies and directives. In addition to reducing handling and waste disposal costs, Navy aircraft and equipment will be properly maintained. This is particularly important considering the cost of these A/C, weapon systems and SE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to many areas of the commercial sector (aerospace, automotive, marine, etc.).

9. Milestones/Accomplishments:

1. Evaluate Alternative Stripping Processes' Parameters	09/93
2. Establish Joint Navy/Air Force Investigation of FlashJet (6" Head)	09/93
3. Evaluate FlashJet Stripping on Metal Substrates	06/94
4. Initiate water-jet stripping evaluation	09/94
5. Optimize FlashJet Stripping Rate (12" Head)	12/94
6. Evaluate FlashJet Stripping on Composite Substrates	01/96
7. Optimize water-jet stripping	06/96
8. Incorporate manipulator head with FlashJet	06/96
9. Service Demonstration of FlashJet	06/97
10. Service demo of water-jet stripping	09/96
11. Transition FlashJet System for Depot validation	09/97
12. Complete Depot Validation of FlashJet System	12/97
13. Implement water-jet stripping (I Level)	09/97

During FY 95, investigation of advanced coatings removal processes led to the implementation of an Ultra-High Pressure waterjet (UHP-WJ)system at Naval Aviation Depot Jacksonville. The

UHP-WJ system removes abrasion resistant metallic/ceramic coatings from Naval aircraft engine components. This system eliminates the need for acid chemical and abrasive blasting stripping of these coatings. The UHP-WJ system filters and recycles its process water and therefore generates near-zero waste. This system will operate on a full production basis in early 1996 and return on investment (ROI) is expected less than six months.

Nine P-3 aircraft were successfully depainted with a non-hazardous air pollutant chemical at Naval Aviation Depot Jacksonville. Data was gathered on the loss of effectiveness below 700 F and the associated waste from this process. In July, 1995, the flash lamp/dry ice prototype process was successfully demonstrated on a Navy F/A-18 radome at McDonnell Douglas Aerospace in St. Louis. Other large parts depainted successfully included: C-17 wing slats, F-15 radome, AV-8B horizontal stabilizers. Also, flash lamp/dry ice materials testing on monolithic composite specimens was completed and data will be available in February 1996. Finally, during December, 1995, the assembly of the Aircraft Depaint Manipulator (ARMS III) was completed. 1 CNO (N-451) Equipment Procurement Funds.

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP in coordination with the Lead Maintenance Technology Center for Environment and the National Defense Center for Environmental Excellence (Waterjet & hand held flashjet). These processes will be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination throughout the development and evaluation of these materials and processes will insure their availability for implementation.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
Navy	185				185
SERDP	445	428	423	930	2,226
TOTAL	630	428	423	930	2,411

12. Performers:

Development of alternative stripping processes is being performed by the Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX) in conjunction with the Naval Air Systems Team and Warner Robins AFB. The NAVAIR Team consists of the Naval Air Systems Command, NAWCADPAX, Naval Aviation Depots (North Island, Cherry Point, and Jacksonville) and the Lead Maintenance Technology Center for Environment. Headquarters, laboratory and field personnel are all supporting this project. This effort is being coordinated with efforts being performed by the Air Force (Tinker AFB, Kelly AFB and Tyndall AFB) and aerospace industry (MDA, Boeing, etc.).

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14. Keywords:

Paint stripping, Materials Substitution, Waste Recycling/Reuse, Flashjet, Waterjet, Plastic Media Blasting (PMB)

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** High-Performance, Lead-Free Electrical Sealants

3. **Agency:** U.S. Department of Energy (DOE)

4. **Laboratory:** Sandia National Laboratories (SNL)

5. **Project ID:** #429

6. **Problem Statement:**

High-performance, electrical-grade polysulfide (MIL-S-8516F) is used extensively throughout the DoD as a fuel-resistant sealant for electrical components in aircraft; it is also used as a sealant by the DOE to protect warhead arming, fusing, and firing sections, which operate at medium to high voltages. However, electrical-grade polysulfide contains lead oxide, a hazardous material that will be subjected to strict Environmental Protection Agency (EPA) regulations in the near future. A lead-free material meeting the high performance DoD and DOE design requirements needs to be found. Finding such a material will help the Pollution Prevention SERDP Thrust Area achieve its objective of reducing the use of lead, one of the hazardous substances targeted by EPA. Work will also be performed to see if toluene sealant solvents, also targeted by the EPA, can be replaced with nonhazardous solvents.

This program would be a continuation of DOE/ECM-funded seed project. The beginning of the program would be applied research to develop a nonhazardous material substitute. This would be followed by technology transfer to both aerospace and DOE-integrated suppliers, contractors, and repair depots.

7. **Project Description:**

Understandably, it will be challenging to find a lead-free sealant that would be a completely compatible drop-in for MIL-S-8516F. This material has been in use for more than twenty years has had many of it's problems ironed out through field experience and constant tweaking. Thus, our first effort will be to develop a viscosity envelope for evaluating the flow of both the lead-containing polysulfide and alternative materials such as lead-free polysulfides and thioethers. Understanding sealant rheology is particularly important to insure that the alternative sealants can fill narrow channels and gaps. Long-term reliability testing will also be required for the new lead-free sealants so that they can qualify for the stated high-performance applications. Stability of the formulated production material needs to be determined in order to determine shelf life, particularly for field repairs. Production lot material identification by "finger printing" should be developed to reduce supplier packaging cost and insure product reliability. We would introduce an innovative procedure for accurately tracking each lot from supplier to government

application. This is based on the work of two of the project participants, Keenan and Shepodd, who have developed material tagging procedures for addressing several national security issues. Better material and process characterization information will be used in the rewriting or issuing of a new specification.

In addition to evaluating polysulfide formulations with non-lead additives, this project will investigate the feasibility of using non-polysulfide formulations. For example, extensive work done by Courtaulds, Inc. indicates that polythoether may be a viable candidate as replacement for the standard polysulfides. The cure rate for this material is easier to control than that of polysulfides because moisture is not part of the curing process. Also, available to other sealant manufacturers.

Finally, we plan to investigate encapsulants that do not rely on toluene solvents. Work performed to date indicates that polythioether may not require toluene solvents.

The major technical challenge in this project is identification of suitable lead-free formulations that can be developed into electrical-grade sealants capable of meeting the stringent requirements of MIL-S-8516F. These formulations have been identified in the project thus allowing further product testing and development, material fingerprinting development, specification development, and commercial source development to proceed.

8. Expected Payoff:

There is a strong likelihood that lead-containing (8516 type) polysulfides will be difficult or nearly impossible to acquire within the next few years because of stricter requirements placed on hazardous waste minimization. Also, vendors are finding it difficult to obtain the proper grade of the required lead peroxide curative. Another issue is the supplier may have to assume cradle-to-grave responsibility (currently under discussion at EPA) for these materials. This project will cooperate with the interested government agencies and vendors in order to develop an environmentally friendly, drop-in material that can provide solutions to these concerns.

9. Milestones/Accomplishments:

1.	Viscosity evaluation incorporated to sealant performance specification	11/95
2.	Lead-free materials identified for testing*	05/96
3.	Material compatibility testing	11/96
4.	Material fingerprinting procedure specified as new method to tag vendor production lots	04/97
5.	Rewrite MIL-S-8516 (a new specification may be issued)	08/97

10. Transition Plan:

Instead of having government laboratories develop a new material by themselves, we would work with up to four potential vendors to formulate a new material. The DoD and DOE facilities would provide specification requirements, extensive testing, general guidance for formulation, and

methods for material control that will lower their production cost. Because of the high performance nature required of these materials, only small-scale private sector, technical dual-use potential is anticipated. When a solvent-free material (late in the program) is developed, applications for a CRADA would assist in the transfer in the use of new generations of sealants to application like sealing and encapsulating concentrator solar assemblies instead of using silicones. This could realize a large material cost savings.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	110	126	230	450	916
DoD	10	50	50	50	30	190
DOE	530	200	250	250	100	1,230
Total	540	360	426	430	580	2,336

12. Performers:

DOE performer is Sandia National Laboratories. DoD performers are the Navy Air Warfare Center in Patuxent River, MD and the Materials Directorate at Wright Patterson Air Force Base. Also the General Service Administration - Federal Supply, in Auburn, WA.
Also the General Services Administration - Federal Supply, in Auburn, WA.

13. Principal Investigator:

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14. Keywords:

Hazardous Waste Generation, Polysulfide, Polythioether, Lead, MIL-S-8516, Sealant, Fuel resistance, Potting Material, Connectors

SERDP FY96 PROJECT

1. SERDP Thrust Area: Pollution Prevention

2. Title: Solvent Substitution and Low VOC Cleaners

3. Agency: U.S. Navy

4. Laboratory: Naval Air Warfare Center Aircraft Division Warminster

5. Project ID: #67

6. Problem Statement:

To identify low VOC (volatile organic compound) content cleaning solvents for use on Navy aircraft (A/C), weapon systems (WS) and ground support equipment (GSE) and to identify replacements for methylene chloride-based chemical paint strippers. Volatile organic solvents such as methyl ethyl ketone (MEK) are used for solvent wipe-down of aircraft prior to painting and post-painting cleanup. Other procedures require the use of stoddard solvent for cleaning aircraft parts in solvent tanks. Other degreasing and cleaning methods use high VOC cleaners. In addition, current chemical paint strippers containing hazardous components (i.e. phenols, methylene chloride, chromates) and paint removal operations at maintenance depots are a major contributor to the hazardous waste generated by the DOD. Recently, OSHA reduced the permissible exposure limit for methylene chloride from 400 ppm to 50 ppm, forcing users to make extensive changes in ventilation and personal protection. The Clean Air and Water Acts, RCRA and local EPA and AQMD regulations limit or prohibit the use/disposal of these hazardous materials. Also, CNO directives require significant reductions in hazardous waste. Therefore, low VOC non-toxic alternative cleaners need to be developed. In addition, there is a need to evaluate alternative chemistries for paint removers for use at Naval Aviation Depots (NADEPs) in order to identify a product or a chemistry capable of satisfying existing and future regulations while maintaining aircraft performance and operational readiness. This effort is covered under the Tri-Service Environmental Quality Strategic Plan; Pillar 3: Pollution Prevention, Requirement Thrusts: 3.1.2.b Non-polluting, Non-toxic Cleaning and Degreasing and 3.1.5.a: Non-Hazardous Paint Removal and is a continuation of an existing 6.2/6.3 effort.

7. Project Description:

Solvent cleaners must be effective on a diverse combination of soils from baked on carbon to aircraft greases and lubricants. This program will identify solvent blend formulations and develop aqueous cleaners which will be evaluated with laboratory performance and cleaning efficiency tests. The best materials will be further evaluated for performance, compatibility, vapor pressure, odor, evaporation rate, safety and cost. Optimized materials will be service tested at a NADEP and transitioned to fleet use through specification modification and design changes. Non-methylene chloride alternatives must exhibit workable performance characteristics while

reducing the impact of stripper waste on disposal operations. Because there are so many different substrates/alloys and coating systems currently used by the Navy, non-hazardous paint removers will also have to be versatile. This program will identify the best alternatives for ambient coating removal operations. Procedure efficiency, effects on substrate surface, hazardous waste generation and applicability will be investigated in order to determine the best procedure for Navy applications. The best alternative material will be demonstrated at a NADEP and transitioned to fleet use through specification modification and design changes.

8. Expected Payoffs:

The development of low VOC solvents would significantly reduce the total amount of hazardous material emissions generated. In addition, the elimination of the methylene chloride based chemical paint strippers would significantly reduce the total amount of hazardous materials generated by Navy maintenance facilities and eliminate the need for expensive emission control equipment ($1M/Facility). This effort is in direct support of Navy and DOD hazardous waste minimization policies/directives. In addition to reduced handling and waste disposal costs, Navy aircraft and equipment must be properly maintained. This is particularly important considering the cost of A/C, WS, and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to commercial aerospace, automotive, and marine industries.

9. Milestones/Accomplishments:

1. Develop/Optimize biodegradable turbine engine cleaners	06/92
2. Evaluate alternative stripper chemistries	09/92
3. Service demo of biodegradable turbine engine cleaners	08/93
4. Initiate low-VOC wheel well cleaner evaluation	09/93
5. Evaluate/optimize stripper process parameters	09/93
6. Initiate non-VOC A/C exterior cleaner evaluation	01/94
7. Develop low-VOC wheel well cleaner	06/94
8. Transition biodegradable turbine engine cleaners	08/94
9. Service demonstration of optimized stripper materials	09/94
10. Initiate tank-type paint stripper evaluation	09/94
11. Develop tank-type paint strippers	06/95
12. Develop non-VOC A/C exterior cleaners	06/95
13. Service demonstration of non-VOC A/C exterior cleaner	03/96
14. Service demonstration of low-VOC wheel well cleaner	03/96
15. Complete demo and spec revision of non-HAP strippers	03/96
16. Write specification for non-VOC A/C exterior cleaner	06/96
17. Implement non-HAP chemical strippers	06/96
18. Write specification for low-VOC wheel well cleaner	06/96
19. Initiate low-VOC pre-paint cleaner investigation	06/96
20. Establish QPL for low-VOC wheel well cleaner	06/96
21. Establish QPL for non-VOC A/C exterior cleaner	09/96
22. Revise tech manuals for low-VOC wheel well cleaner	09/96

23. Implement optimized low-VOC wheel well cleaner	09/96
24. Revise tech manuals for non-VOC A/C exterior cleaner	12/96
25. Implement tank-type paint strippers	12/96
26. Implement no VOC A/C exterior cleaner	03/97

Several biodegradable turbine engine cleaners were evaluated at NAWC Warminster. Top performers were successfully field tested at NAWC Trenton. These new products were implemented through changes in MIL-C-85704.

Non-Hap chemical strippers were evaluated at NAWC Warminster. One promising candidate was successfully field tested at NADEP Jacksonville. A new military specification was prepared for these materials. An evaluation of the hydrogen embrittlement potential of these materials is currently in progress and must be completed before final implementation.

A non-VOC aircraft exterior cleaner has been developed at NAWC Warminster/Patuxent River which exceeds the requirements of the current specification. This product will proceed into the demonstration/validation phase 3Q FY-96. MIL-C-85570 Type II will be revised to implement this product.

A low-VOC wheel well degreaser has been developed at NAWC Warminster/Patuxent River. This product will proceed into the demonstration/validation phase 3Q FY-96. MIL-C-85570 Type V will be revised to implement this product.

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through the Lead Maintenance Technology Center for Environment (LMTCE). These materials will then be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials and processes will insure availability for implementation.

11. Funding: $K

	FY94	FY95	FY96	FY97	TOTAL
SERDP	150	99	121	350	720

12. Performers:

Development of non-methylene chloride paint strippers is being performed by the Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX) and coordinated with NADEPs and the Air Force (Kelly AFB and Warner Robins AFB). The solvent substitution and low VOC cleaner efforts are being performed by NAWCADPAX, NADEPs, and the LMTCE and are being

coordinated with efforts by the Air Force (Tinker AFB, Kelly AFB, and Tyndall AFB), DOE and, aerospace industry (Boeing, etc.).

13. Principal Investigator:

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14. Keywords:

Solvents, Chemical Paint Strippers, Materials Substitution, Cleaners, Volatile Organic Compounds, Methylene Chloride Replacement

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Laser Cleaning and Coatings Removal

3. **Agency:** U.S. Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)

5. **Project ID:** #139

6. **Problem Statement:**

The goal of the proposed effort is to provide a field demonstration of a prototype laser-based facility to demonstrate environmentally acceptable component cleaning and coating removal technology and to transition it to aerospace users, including the following Air Force Logistic Centers:

Oklahoma City Air Logistics Center (OC-ALC)
San Antonio Air Logistics Center (SA-ALC)
Warner Robbins Air Logistics Center (WR-ALC)
Sacramento Air Logistics Center (SM-ALC)
Ogden Air Logistics Center (OO-ALC)

Cleaning and coatings removal technologies have traditionally depended upon the use of organic solutions, such as, PD 680 (I, II, & III) methyl ethyl ketone (MEK), methylene chloride (MECL), phenol, and strong acids and bases as well as hot potassium permanganate solutions. These materials are hazardous, and include volatile organic compounds (VOCs), ozone depleting chemicals (ODCs) and air toxic emitters which are subject to severe restrictions or are being banned altogether, such as freon (CFC-113). More recently, the trend in cleaning technology is toward the use of water based cleaners (sodium metasilicate bases, terpene/water emulsions or water detergent blends), some of which may be hazardous to some degree. However, technologies are needed which do not involve generation of waste water streams.

Laser-based cleaning and coating removal has been demonstrated to be an environmentally acceptable, affordable and controllable technology. A demonstration facility is needed to facilitate transition of this technology to Air Force, DoD and industry use, targeted to the immediate needs of the Air Logistics Centers.

This is the continuation of an FY93 SERDP funded program.

7. Project Description:

The project objective is to demonstrate the use of laser cleaning and coating removal on components ranging from turbine engine blades to landing gear and radomes.

The project approach is to design, fabricate, test, evaluate and demonstrate a state-of-the-art automated, controllable laser cleaning and coating removal facility. The facility will be designed for carbon dioxide and eximer laser cleaning and coating removal operations. System operation will be fully robotized and computer controlled with on-line instrumentation for component positioning and measuring and controlling laser inputs to the part surfaces.

The project involves the following tasks:

Design system to demonstrate technology on aircraft components.

Design a subsystem system to handle, treat or capture, as necessary, all gaseous and particulate products of the process.

Purchase or fabricate lasers, computers, robotics, controller, sensors, hardware and software necessary for the operation of the system.

Assemble the demonstration facility system. Make necessary mechanical hardware and software modifications to insure safe, reliable and controllable operations.

Demonstrate system on both metallic and non-metallic specimens.

Test and evaluate adequacy of cleaning and coating removal process for aircraft components. Operate the facility and make it available for ALC and GOCO engineering evaluation on specific aircraft components.

Qualify facility to applicable specifications for aircraft components cleaning and coating removal.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort also will enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment. This program supports the DoD objectives to reduce volatile air emissions by 50% by the end of 1999 (1993 baseline).

Extensive test and evaluation work has been completed by the Air Force and the Navy on laser radiation effects on substrate materials and coating removals. What is needed next is a prototype facility where test and evaluation cost analysis and cleanliness levels can be performed on a variety of aircraft components. The facility would be available to the services as well as the aerospace community for test and evaluation purposes.

The technical risks involved in this project are low. Industrial lasers, both carbon dioxide and eximer are available; controls, robotics sensors, instrumentation are also available. Software will

have to be developed/modified to control the production system. Systems design must incorporate all applicable safety devices and features.

Tie to Tri-service Environmental Quality R&D Strategic Plan
Pillar Thrust Area: 3.B.2
Requirements Category: 3.I.5.a
Work effort: Tech Base

8. Expected Payoff:

The laser based cleaning and coating removal facility will be applicable to a broad range of aircraft and general equipment cleaning and coatings removal work. Benefits include the complete elimination of the use of toxics and hazardous waste generation in logistic center maintenance and re-manufacturing operations relying on the new technology. The limits of such potential payoff are presently unexplored and remain to be determined. The process is expected to be highly cost effective considering that all costs for hazardous materials management and management of solid, liquid, and vapor waste streams will be eliminated.

9. Milestones/Accomplishments:

1. Project Initiation/begin assessment	04/94
2. Complete assessment	12/94
3. Report/document recommendations and findings	04/95
4. Contract award and begin final design	06/95
5. Approve Design and initiate hardware procurement/component fabrication	06/96
6. Initiate life cycle cost study	06/96
7. Initiate systems assembly and check-out operations	11/97
8. Complete check-out and de-bug of systems operations	05/98
9. Initiate test and evaluation with services and industry customers	06/95
10. Complete life cycle cost studies and economic benefit studies	11/98
11. Final report and transfer of system to selected DoD facility (ALC)	12/98

The resulting facility will totally eliminate the use of many of the chemicals needed for present depot level maintenance. It will also reduce the quantity and frequency of use of many other chemicals thereby significantly reducing the overall waste stream from depot facilities.

10. Transition Plan:

It is planned that the system to be built under this effort will be a prototype demonstration and as such will have many more capabilities than required on an actual production system. Users will perform test and evaluation programs on the prototype and determine the capabilities needed for their production unit. Cost data will be generated, specific engineering problems will be addressed and production systems design requirements will be generated.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	300	1,552	0	15	1,500	950	4,302

12. Performers:

The project will be performed under the technical leadership and direction of the Air Force Material Command, Aeronautical Systems Center, Wright Laboratory, Materials Directorate, Wright-Patterson AFB, OH 45433.

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Manufacturing Technology Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

13. Principal Investigator:

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14. Keywords:

Cleaning, Coating Removal, Lasers, Methylene Chloride, Methyl Ethyl Ketone, Phenols

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Large Area Powder Coating

3. **Agency:** U.S. Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)

5. **Project ID:** #121

6. **Problem Statement:**

Current surface coating technologies for aerospace systems employ spray application processes which use and release volatile organic compounds (VOCs) or Isocyanates. Existing primers and topcoats are solvent based systems which have offered excellent protection against corrosion or other operating environment conditions. However, industrial use of solvent based technology has numerous drawbacks: evaporation of toxic volatile organic compounds (VOCs), release of toxic isocyanates, low transfer efficiency, and relatively long cure times. An alternative technology, use of powder coatings, has generated considerable interest within the aerospace industrial community. Powder coating typically involves electrostatic application of powdered metal to a grounded part, followed by a curing cycle to flow the material into a continuous coating. Advantages of powder metal technology include: some reduction of toxics used and generated, increased transfer efficiency, and reduced costs of environmental safety and compliance. Another method is to heat the part and immerse it in a bed of powder and then heat cure it. Current technology has limitations, however, in use of powder for large parts, such as those on the outer moldline of aircraft; overheating of parts, and film properties. Technology development is needed to obtain the full benefit of powder coatings use in this area of aerospace manufacturing.

7. **Project Description:**

Technical Objective: Technology for large area powder coating will be developed, optimized, reduced to practice, and qualified for use on Air Force systems.

Technical Approach: This program is an integrated program to develop alternatives to solvent based coating systems for large aircraft parts. Considerations in identifying an acceptable technology will include: maintenance or improvement of substrate integrity, effects of part geometries, process quality assurance, and curing specifications. Candidate technologies, including both government and industry initiatives, will be identified and assessed. Development needs will be identified and implemented. Most promising technologies will be developed, optimized, scaled-up, demonstrated and qualified. Needs of Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

The planned effort will be coordinated with Wright Laboratory continuing work on advanced low VOC and powder coating programs and a highly requested part of the AFMC and used approved "Air Force Paint Strategy".

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment.

The proposed effort is relevant to various Air Force and industry efforts to develop powder metal technologies for aerospace use. The needs of ALCs are sufficiently urgent to warrant Wright Laboratory participation in the quest for acceptable large area powder coating technology.

Tasks/activities: Process studies will be conducted to identify and assess candidate technologies, including both government and industry initiatives. Studies of development needs will be identified and implemented. The most promising candidate technology will be selected for testing, analysis, development, optimization, scale up, demonstration and qualification. Life cycle cost studies will be performed. The prototype will be transitioned to users for extended production evaluation. The needs of ALCs and GOCOs will be given priority attention.

Technical issues to overcome: Major technical issues include: powder formulation/curing optimization, handling and storage, 500 MPH rain erosion and maintenance of proper coating quality and thickness.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.B.1
Requirements Category:	3.I.4.a
Work effort:	Tech Base

8. Expected Payoff:

Availability of acceptable large area powder coating technology will liberate Air Force and industry users from the burdens of using a technology dependent on VOCs and air toxics. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, the burdens of environmental compliance and costs of hazardous materials and waste management and response will be entirely eliminated.

The planned effort will not adversely impact system efficiency, capability, or schedule. Experience with detail part technologies suggests that costs may be lower.

9. Milestones/Accomplishments:

1. Project studies defined powder coating process mechanisms and requirements for large area coating. Demonstration site selected and prototype team has been mobilized. Materials properties tests and

experiments have been designed and completed.
2. Definition studies are complete. Parts and processes to be targeted for development and application of the new technology have been selected. Experimental design for initial technology demonstration initiated.
3. Initial deposition demonstration produced a process and coating that meets 90% of objective goal in performance. Many objectives were surpassed (exceptional adhesion and corrosion resistance), but noise level, diffuseness and 500 MPH rain erosion need further optimization.
4. Optimization of powders thermal spray and durable/cleanable low VOC conventional coatings initiated.
5. Initial powders formulated into durable/cleanable low VOC conventional coatings show lower VOCs and improved performance
6. Powders optimized for durable/cleanable low VOC conventional coatings
7. Powders optimized for thermal spray coatings
8. Finalize field deposition technology demonstration agenda. Site selected for deposition demonstration. Initiate preparations for technology demonstration.
9. Conduct deposition technology demonstration. Initiate analysis of results in concert with research partners and user technical representatives
10. Completed review of initial technology demonstration results. Initiate validation and optimization studies . Initiate experiments to determine effects of processes on substrates/parts. Evaluate process quality and consistency.
11. Complete validation and optimization prototype studies. Initiate planning for scale-up studies. Determine full scale process requirements in terms of equipment, personnel, siting, and operating processes.
12. Complete scale-up planning. Initiate acquisition and positioning of scale-up elements.
13. Conduct pilot scale demonstration. Review results and determine of full implementation is appropriate.

BBM has started formulating coating systems with promise of superior durability. General Atomics has produced some new powders for improved properties. The Warner Robins ALC personnel participated in High Velocity Thermal Spray sample Spray trials at Aeroplas, Hollis, NH. Nylon 11 samples were sprayed. Plans for field demo on missiles were discussed. The 500 MPH rain erosion data presented showed exceptional performance for an uncrosslinked resin system. This surrogate system performance appears to be sufficient for many applications. Crosslinked systems are under development for aircraft.

10. Transition Plan:

Following the decision to perform full scale demonstration, a demonstration plan will be developed in concert with the user for the selected demonstration site (ALC or GOCO). Performance testing parameters will be developed, equipment and materials procured and positioned, and staffing and support arranged. Full scale demonstration will then be conducted. Findings will be compiled and made available to prospective users for review and evaluation. After evaluation and acceptance, specifications and standards will be prepared or revised to make the new technology available for production or logistics use.

Degree of coordination conducted between performer and user: Potential users will be an integral part of the R&D effort for its duration. Their participation an technical inputs will be utilized throughout the technology development and validation process.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	100	315	0	264	215	894

12. Performers:

The project will be performed under the technical leadership and direction of:

Air Force Material Command
Aeronautical Systems Center
Wright Laboratory
Materials Directorate
Wright-Patterson AFB, OH 45433

The Materials Directorate has awarded multiple research contracts to industry to perform the development and integration tasks.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the pilot and full demonstration site to be either an Air Force Material Command Air Logistics Center, the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB, Ohio, or a selected Air Force GOCO facility. Two ALCs have volunteered. Currently Warner Robins ALC is the selected site and are participating.

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Wright Laboratory has extensive research and development experience in the area of durable/cleanable coatings and application and fusing of powdered thermoplastic materials on metallic/non-metallic substrates. Wright Laboratory also has extensive long term research and development experience with powder and other coatings technology. Many of the DoD specifications involving coatings technologies have been developed by and are under the jurisdiction of Wright Laboratory.

14. Keywords:

Coating, Powder Metallurgy, VOCs, Isocyanates, Air Pollutants, Painting

SERDP FY 96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Rapid Testing for Acceptable Materials and Processes

3. **Agency:** U.S. Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)

5. **Project ID:** #117

6. **Problem Statement:**

The goal of this project is to develop low risk, fast track methodologies and techniques for military qualification of new or modified environmentally benign materials.

Continuing efforts to develop environmentally acceptable materials and processes are constrained by the time-consuming process of qualification testing. Users (customers) must make their decision under conditions of uncertainty and want to take as low as risk possible in the decision. Frequently, substantial testing was conducted in support of the initial product qualification decision or in support of requalification for design modification to improve performance or solve problems. The present qualification test process is both time consuming and costly and is often preempted by environmental compliance or enforcement requirements.

There is a real need to develop accelerated and less costly means for qualification testing of alternate, substitute and emerging new materials and processes in order to rapidly introduce environmentally acceptable materials into the military inventory and force structure. Economical means are required in order to preserve a diminishing source base threatened due to costly restrictions.

7. **Project Description:**

Technical Objective: The objective is to develop low risk, fast track methodologies and techniques for military qualification of new or modified environmentally benign (low volatile organic compound (VOC) and nonchromated) adhesive and adhesive primer materials as well as environmentally benign metal prebond surface preparations. The goal is to create combined environmental and reliability test techniques with 20:1 time compression ratio for evaluating adhesive bond durability.

Technical Approach: This is an applied research effort which will transfer to the Air Force Logistics Centers (ALCs) and their contractors. Existing long-term (10+ years) exposure data available for adhesively bonded joints which were prepared using state-of-the-art technology will be used as the baseline for this program. Extensive evaluation of these data (particularly the

failure modes of the exposed bonded joints) led to some preliminary conclusions as to the mechanism by which the actual bonds were degraded over time. The 10-year data will be duplicated in an accelerated fashion by using laboratory test techniques and aging environments believed to be pertinent for evaluating the mechanism determined to be at work in the baseline specimens. The testing regimen will be optimized and the results will be compared to the baseline. Factors expected to influence the degradation mechanism, such as aluminum grain boundary structure and adhesive primers, will be investigated. The material aging physics will be characterized and a theoretical bridge between actual long-term testing and the accelerated testing will be developed.

Industry experts currently employing long-term testing (greater than 1 year) as a requirements for qualification of new adhesives and surface preparations will participate in the program as technical consultants and will also provide specimens and testing for comparison of their long-term testing with the accelerated tests developed.

Adhesive bonded components removed from flying or retired aircraft will be obtained. Good and debonded area will be characterized, with good areas being machined into specimens for testing. Correlation will be made between accelerated testing and actual service history. Significant in-service durability data available for existing bonding processes will also be correlated with accelerated testing conducted using specimens prepared with these processes. Additional long-term exposure specimens will be obtained from industry, and results will be compared to the accelerated test data generated during this program. Additional specimens will also be placed in long-term exposure so future direct comparisons will be possible with the new accelerated test techniques.

The major technical risks are as follows: (1) duplicating the end effect and mechanisms of long-term aging on bonded joints and (2) determining and generating the amount of empirical evidence required to support configuration change decisions.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.J
Requirements Category:	3.III.2.f
Work effort:	Tech Base

8. Expected Payoff:

Potential users include aerospace manufacturers, Air Logistics Centers, Integrated Weapon System Program Offices, and DoD industrial operations. Professional societies such as American Society for Testing and Materials (ASTM) will be invited to participate in reviewing project plans, progress, and results. The development of an acceptable accelerated testing technology will reduce time for testing, reduce cost of testing, and eliminate costs of environmental compliance and hazardous materials/waste management. These efficiencies and economies will result from elimination of unnecessary or redundant tests and earlier implementation of clean technology.

9. Milestones/Accomplishments:

1. Initiate project - begin studies to select target materials and testing requirements	03/94
2. Target materials and tests isolated	05/94
3. Contract award - initiate studies of failure modes and test modes	08/94
4. Failure modes identified - test modes identified	11/94
5. Aging physics identified	03/95
6. Theoretical bridge established	05/95
7. Peer review	06/95
8. Advanced testing techniques selected	08/95
9. Identify and acquire materials for primer and grain boundary studies	08/95
10. Complete specimen fabrication for primer and grain boundary studies	09/95
11. Identify candidate parts for use in correlation with actual service history	11/95
12. Complete mechanical testing for primer and grain boundary studies	12/95
13. Refine theoretical bridge if necessary	12/95
14. Initiate ATTD/MT planning as required	12/95
15. Prepare specimens and conduct tests for round robin testing with industry adhesive primer team	02/96
16. Complete data analysis and micrographic examinations for primer and grain boundary studies	03/96
17. Obtain parts for use in correlation with actual service history	04/96
18. Complete all testing and data analysis	06/96
19. Demonstrate advanced techniques and correlate test results with historic data	08/96
20. Release technology transfer media	09/96

A corrosion mechanism was identified as the primary factor in degradation of the baseline long-term bonded joints. Laboratory accelerated tests were generated using techniques known to instigate the type of corrosion identified. Several testing regimens were evaluated, and two promising test methods were identified. Results duplicating the baseline using these two tests have been generated during two separate tests.

The industry support team is extremely encouraged by the results to date, and have fabricated specimens for testing. They will also test other specimens using their existing long-term techniques in order to begin to generate the data they will need to supplant their testing with the new accelerated methods.

10. Transition Plan:

An ad hoc group consisting of various aerospace industry and adhesive industry representatives has been formed to support this project. This group will provide advice and act as a "sanity check" for the program. They will also be key to transition of the technology since they are the current users of the long-term tests which must be replaced by the accelerated methods.

When the advisory group is satisfied the accelerated test methods are feasible and they decide to implement them, the testing techniques will be formalized through the American Society for Testing and Materials (ASTM) or other appropriate vehicle. Initial implementation will likely be to supplement rather than replace existing test methods. As more confidence is gained that the theoretical bridge between the long-term and accelerated tests is sound, the long-term tests will be discontinued.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	100	263	118	144	625

12. Performers:

The project will be performed under the technical leadership and direction of:

Air Force Material Command
Aeronautical Systems Center
Wright Laboratory
Materials Directorate
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration. Loral Vaught Systems will be a key participant since they generated the long-term testing used as a baseline for this project.

13. Principal Investigator:

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14. Keywords:

Qualification Testing, Age Testing, Adhesive Bonding

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Capacitive Deionization for Elimination of Wastes (Efficient Treatment of Wastes with Carbon Aerogel Electrodes)

3. **Agency:** U.S. Department of Energy (DOE)

4. **Laboratory:** Lawrence Livermore National Laboratory (LLNL)

5. **Project ID:** #436

6. **Problem Statement:**

Ion exchange is now used as a means for removing anions and cations, including heavy metals and radioisotopes, from process and waste water in various industries. Unfortunately, ion exchange produces a tremendous amount of chemical secondary waste during regeneration. LLNL has recently developed an innovative new technology, carbon aerogel capacitive deionization (CDI), that can be used to replace ion exchange. This innovation was recently awarded an RD100 Award and has been issued a patent (U.S. Pat. No. 5,425,858). Carbon aerogel CDI is electrically regenerated and eliminates the secondary waste associated with ion exchange. Unlike reverse osmosis and electrodialysis, there are no troublesome membranes to undergo chemical and radiation-induced degradation. Aqueous solutions with various anions and cations are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m2/g). After polarization, non-reducible and non-oxidizable ions are removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes. As desired, the effluent from the cell is purified water. This process is also capable of simultaneously removing a variety of other impurities. For example, dissolved heavy metals and suspended colloids can be removed by electrodeposition and electrophoresis, respectively. Carbon aerogel CDI can produce a continuous flow of product water by operating two stacks of carbon aerogel electrodes in parallel. One stack purifies while the other is electrically regenerated. This mode of operation is called potential swing and also enables energy recovery. For example, energy released during the discharge of one stack of electrodes (regeneration) can be used to charge the other stack (deionization). Such synchronous operation requires user-friendly automation. This level of automation and sophistication has been incorporated into the demonstration process now available at LLNL.

7. **Project Description:**

Proof-of-principle and parametric studies have been completed. It has been shown that non-oxidizable, non-reducible nitrate, perchlorate, phosphate, sulfate, carbonate, and chloride salts can be removed from electrolytes. Experiments have been conducted at solution conductivities

ranging from 7 to 10,000 mS/cm. Most experiments were performed at 100 to 1000 mS/cm. During cell testing, we have recently demonstrated that the electrochemical cells with carbon aerogel electrodes can be used to effectively remove a variety of heavy metals including copper, manganese, zinc, cadmium, cobalt, chromium, lead, and uranium from aqueous process streams and natural waters. Treatability tests on ground water at LLNL have shown that chromium contamination can be reduced to 2 ppb, well below the acceptable level of 11 ppb.

A fully-automated industrial-grade control system has been developed. It is implemented using a 486DX 33-megahertz computer with 16 megabytes of memory and a 340 megabyte hard disk. A 21 inch high resolution color monitor serves as the operator display. Operator input is via a mouse and keyboard. The operating system is DOS v6.22 running Windows v3.1. A single AT-MIO-16DH data acquisition board, installed in the computer, provides the interface to the Input-Output (I/O) Signal Subsystem. The I/O subsystem consist of a single 12-slot Signal Conditioning Extension Interface (SCXI) chassis. The chassis contains seven 8-channel analog-to-digital (A/D) modules to measure flow, level, pressure, temperature, pH, and conductivity; two 16-channel single-pole double-throw (SPDT) relay modules for controlling pumps and valves; and one 6-channel digital-to-analog (D/A) module for controlling power supply voltages and pump speed. The SCXI hardware provides multiplexing, filtering, isolation, and amplification for the process signals. LabVIEW v3.1 software, running under Windows, is used for data acquisition and control. LabVIEW is a graphical programming environment which provides integrated tools for acquisition, control, analysis, and presentation, as well as connectivity to serial, parallel, voltage, current loop, RTD, thermistor, and relay communication interfaces. Data acquisition and control software is optimized and converted to compiled run-time code. This control system can be used for a small plant (hundreds of gallons per day) or a very large plant (millions of gallons per day). Given the relatively advanced state of development of this process, there is a high probability that it can be deployed at DOD and DOE sites within three years.

Thus far LLNL has completed production of 1555 ft2 (3500 8" x 8" sheets synthesized and pyrolyzed). An additional 222 ft2 has been synthesized by LLNL and awaits pyrolysis (500 8" x 8" sheets). We believe that enough additional material has now been made by Aerojet to meet our first 2000 ft2 milestone. We now have working plastic-aerogel prototypes that use small sheets of aerogel.

8. Expected Payoff:

CDI has several potential advantages over other more conventional technologies. Unlike ion exchange, no acids, bases, or salt solutions are required for regeneration of the system. Regeneration is accomplished by electrically discharging the cell. Therefore, no secondary waste is generated. In contrast to thermal processes such as evaporation, CDI is much more energy efficient. Since no membranes or high pressure pumps are required, CDI offers operational advantages over electrodialysis and reverse osmosis (RO).

At the present time, there is no acceptable means of disposing of mixed wastes produced by ion exchange processes within the nuclear industry. Disposal of hazardous chemical wastes produced

by the regeneration of ion exchange processes in the metal finishing industry is very expensive. For example, the disposal costs for regeneration of a single pound of ion exchange resin in California are approximately $108. This cost would be avoided by carbon aerogel CDI.

Carbon aerogel capacitive deionization is inherently energy efficient. The energy required by this process is approximately QV/2 plus ohmic losses, where Q is the stored electrical charge and V is the voltage between the electrodes. It is assumed that ohmic losses, parasitic electrode reactions, and leakage currents are kept to a minimum. For example, the minimum theoretical work required by an isothermal process to separate a 1000 ppm NH4ClO4 solution into a 1 ppm product stream and a 95,000 ppm concentrate stream is approximately 1.6 J mol-1 (0.1 Wh gal-1), assuming that the NH4ClO4 obeys the Debye-Huckel activity coefficient model. The minimum electrical energy required for charging a CDI cell with NH4+ and ClO4- is 4.4 J mol-1 (0.26 Wh gal-1) at 0.6 V and 9.0 J mol-1 (0.52 Wh gal-1) at 1.2 V. If stored electrical energy is reclaimed during regeneration, or electrical discharge, energy requirements can be reduced to levels well below these. It is much more energy efficient than competing thermal processes such as evaporation. It is extremely competitive with the most efficient reverse osmosis processes. Unlike ion exchange, no high pressure equipment or cold storage of membranes is required. Possible applications of carbon aerogel CDI include: (1) removal of heavy metals and radionuclides from aqueous waste streams; (2) removal of hexavalent chromium contamination from ground water at LLNL; (3) removal of heavy metals and salts from water at Berkeley Pit in Butte, Montana; (4) recycle of water for bioreactors used to destroy chemical warfare agents at Aberdeen Proving Grounds; (5) removal of ammonium perchlorate from waste streams produced by decommissioning solid propellants; (6) preconcentration of trace heavy metals and radionuclides for detection by gamma ray spectroscopy and X-ray diffraction; (7) energy efficient desalination of brackish water for water reclamation; (8) energy efficient desalination of sea water; (9) desalination units with unlimited shelf life for military; (10) electrically-regenerated water softeners; (11) production of ultra pure water for biotechnology and semiconductor processes; (12) treatment of boiler water for fossil and nuclear power plants. In treatability tests at LLNL, it has been shown that hexavalent chromium in LLNL ground water can be effectively removed by carbon aerogel CDI. The process lowered concentrations from 32 ppb to below 2 ppb, well below the acceptable level of 11 ppm. Continuous centrifugation is probably the best and most obvious separation technique for removing suspended solids from an aqueous stream. Once the solids are separated, it will be necessary to use water to wash the solids. The washing process will result in the contamination of the rinse water with various radionuclides which will include ionic forms of 90Sr, 60Co, 134Cs, and 137Cs. Ordinarily, ion exchange might be used to remove such radioactivity from the rinse water. Deionizers based on columns of ion exchange resin and inorganic ion exchangers were evaluated for the removal of 137Cs, 90Sr, and 125Sb from contaminated water at the Three Mile Island Nuclear Power Station Unit No. 2. During plutonium processing, resins and solutions of HNO3 become contaminated with PuO22+ and other radioisotopes. In this case, every kilogram of cation exchange resin requires approximately 100 kilograms of 10 wt. % HNO3 and 2 to 3 kilograms of rinse water for regeneration. Similarly, every kilogram of used anion exchange resin requires approximately 100 kilograms of 10 wt. % NaOH and 2 to 3 kilograms of rinse water for regeneration. Carbon aerogel CDI can be used as an electrically-regenerated alternative to ion exchange. This alternative would avoid generation of chemical wastes during regeneration.

9. Milestones/Accomplishments:

FY93 Milestones	Planned	Rescheduled	Completed
1. Model development	12/93	Continuing	Continuing
2. Design of proof-of-principle system	01/94	01/94	01/94
3. Procure and fabricate hardware	02/94	02/94	02/94
4. Synth. of carbon aerogel for electrodes	03/94	03/94	03/94
5. Measurement surface charge density	04/94	Continuing	Continuing
6. Construct proof-of-principle system	05/94	05/94	05/94
7. Testing of fluid systems	06/94	06/94	06/94
8. Testing of electrical systems	06/94	06/94	06/94
9. Experiments w/ symmetric electrolytes	07/94	Continuing	Continuing
10. Model verification	08/94	Continuing	Continuing
11. Documentation	09/94	Continuing	Continuing

FY94 Milestones	Planned	Rescheduled	Completed
1. Mixed-electrolyte treatability studies	12/94	Continuing	Continuing
2. Design of continuous flow potential swing system	12/94	09/94	09/94
3. Procure and fabricate hardware	03/95	12/94	12/94
4. Synth. of 1st batch of aerogel powder	02/95	Canceled	Canceled
5. Construct continuous flow potential swing system	06/95	01/95	01/95
6. Fluid-flow & electrical subsystem tests	07/95	01/95	01/95
7. Demonstration with NaCl solution	08/95	04/95	04/95
8. Parametric studies w/ simulated wastes	09/95	08/95	08/95
9. Documentation	09/95	09/95	08/95

FY95 Milestones	Planned	Rescheduled	Completed
1. Technology transfer activities	9/95	none	9/95*
2. Optimization aerojel production process	9/95	10/95	11/95**
3. Complete aerogel production 2000 ft2	10/95	11/95	11/95** 4. Complete
aerogel production of 4000 ft2	11/95	12/95	
5 Construction larger capacity CDI stacks	02/95	02/96***	
6. Testing enhanced CDI system at LLNL	01/96	04/96***	
7. Documentation of results	02/96	06/96***	

* Publicity by LLNL has generated interest in U.S. industry. RD100 Award.
**Completion of approximately 2000 ft2 at both LLNL and Aerojet.
***Milestones that will have to be met without SERDP funding.

FY96 Milestones	Planned	Rescheduled	Completed
1. Documentation of All Results	11/95	09/96	
2. Documentation of Hardware	12/95	09/96	
3. Documentation of Software	01/96	09/96	
4. DOE Site Demonstration	06/96	04/96	
5. Documentation of Demonstration	09/96	05/96	

Major accomplishments: 1) successful proof-of-principal for carbon aerogel CDI process; 2) U.S. patent granted; 3) preliminary economic analysis; 4) development of fully-automated, continuous flow, potentia-swing CDI process; 5) initiation of technology transfer step; 6) publication of reports and manuscripts; 7) presentations at EPRI and ASME International Conferences on Low Level Wastes; and 8) RD100 Award won in 1995.

10. Transition Plan:

A site demonstration at LLNL Treatment Facility C will be conducted in FY96. The objective is to remove hexavalent chromium from contaminated ground water. Discussions have also been conducted with both Tyndall AFB and McClellan AFB regarding on site demonstrations. There are tentative plans for a demonstration with plating shop rinse water at McClellan AFB. The geographic location of this site, a few hours from Livermore, will facilitate this collaboration. Cells with ion exchange membranes. No electrode separator was used in the experiments with heavy metals. Consequently, regeneration is difficult. By incorporating an anion exchange membrane between anodes and cathodes, complete electrode regeneration by stripping is possible. Additional funding to pursue our work on heavy metals. Funds needed: $250K.

The initial proof-of-principle system had only 40 ft2 of carbon aerogel sheet at a cost of $5600/ft2. Note that this is not active surface area. The total active surface area was approximately 2.2 x 109 cm2. We are completing the production of 4000 ft2 of high quality carbon aerogel at a cost of only $20/ft2. Additional funding is needed to incorporate this carbon aerogel into large-scale electrochemical cells. Funds needed: $400K.

Additional engineering evaluation. Additional economic studies of the process are needed. A portion of such studies will be sub-contracted to a suitable engineering firm. Funds needed: $200K.

Studies of the chromatographic separation of 14C, 99Tc, 90Sr, 60Co, 106Ru, 134Cs, 137Cs 144Ce, 154Eu, 155Eu, 239Pu, and 241Am from aqueous streams by carbon aerogel CDI will be conducted. Transients in solution concentration, as well as the inventory of radioisotopes electrosorbed on the surface of the carbon aerogel, will be monitored in real time. Funds needed: $500K.

Several water authorities in California, including those in San Diego, Carlsbad, and Alameda County have expressed sincere interest in the possibility of eventually using carbon aerogel CDI for desalination applications. Senator Paul Simon, Congressman Bill Baker, and Representative Dominic Cortese have had briefings on the technology and are all very supportive.

A number of respected private companies have contacted LLNL with interest in licensing carbon aerogel CDI technology for waste and water treatment. It is believed that such contacts will result in efficient technology transfer.

11. Funding: $(K)

In FY93 $795K was allocated for proof-of-principle. An additional $300K was allocated for a preliminary economic analysis of the process. In FY94 $700K was allocated for the development of a fully-automated, continuous-flow, potential-swing CDI process. In FY95 $90K was received in FY95 to promote technology transfer to private industry. An additional $210K of FY95 funding is being used for the enhancement of an existing potential-swing CDI system by increasing its capacity so that it can be used for demonstration at a suitable DOE or DOD site. Approximately $150K has been committed to the large-scale production of carbon aerogel at both Aerojet and LLNL. Approximately $60K is being used at LLNL to optimize the aerogel production process, to develop less expensive CDI cells that can be constructed from plastic and aerogel alone, and to test the new cells. An additional $450K has been requested from SERDP for FY97 to enable completion of the project, but has not yet been awarded. Funding will also being sought from other DOD and DOE sources.

	FY93	FY94	FY95	FY96	TOTAL
SERDP	1,095	700	300	560	2,655
DOD	0	0	125	0	125
LLNL	0	0	0	100	100
TOTAL	1,095	700	425	660	2,880

12. Performers:

LLNL is a DOE laboratory operated by the University of California and will be responsible for successful completion of the proposed work. This laboratory has recently developed several novel electrochemical processes for the treatment and destruction of mixed wastes. The Principal Investigator has appropriate experience in electrochemical engineering and process development.

13. Principal Investigator:

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14. Keywords:

Deionization, Ion Exchange, Waste Minimization, Supercapacitor, Aerogel, Potential-Swing, Capacitive Deionization.

SERDP FY96 PROJECT

1. SERDP Thrust Area: Pollution Prevention

2. Title: Acid Recycle

3. Agency: U.S. Department of Energy

4. Laboratory: Los Alamos National Laboratory (LANL)

5. Project ID: #422

6. Problem Statement:

Field demonstrations will be conducted at the Los Alamos Plutonium Facility to recycle and reconcentrate nitric and hydrochloric acids from plutonium-containing liquid waste streams. Nitric acid and hydrochloric dissolution of plutonium-containing solids is a baseline technology for plutonium processing operations. Following removal of plutonium from the acid solutions, previous operations neutralized the acid with caustic and discarded it as waste. Most of the nitric or hydrochloric acid could be separated from the waste solutions and recycled, thus reducing amount of waste generated. This in process technology can also provide major reductions in nitrates and chlorides in effluent streams from processing aimed at cleanup of residues from previous operations. Recycle of nitric acid will be accomplished via an enhancement of capabilities in the existing nitric acid evaporator system. Recycle of hydrochloric acid represents a new program to be implemented, and hardware will be used to augment the Los Alamos aqueous chloride processing system.

7. Project Description:

We will demonstrate at least 95% recycle of nitric and hydrochloric acid from waste solutions. The recycle acid will be reconcentrated sufficiently to be used for dissolutions, etc. in lieu of makeup acid. We will demonstrate nitric and hydrochloric acid recycle from actual plutonium processing waste solutions using two operations:

(1) evaporation of acid from a solution containing radionuclides and inorganic salts and (2) fractional distillation or membrane separation of evaporator product to generate concentrated acid. The acids will be separated from the radioactive component of the waste solution by evaporation. The nonvolatile radioactive residue will be sent to disposal or may receive further treatment (e.g., thermal denitration) before disposal. Evaporated acid will be reconcentrated to a reusable state by fractional distillation. We will develop integrated processes consisting of evaporators followed by enrichment units (distillation columns or

membrane separators). These processes will operate in semi-continuous manner.

Existing nitric acid evaporators will be operated for additional experience. A nitric acid distillation column will be designed, built, and cold-tested prior to incorporation into the plutonium facility. Process flow balance and characterization of hydrochloric acid processes will be done. Bench-scale, "cold" evaporation and distillation experiments will be done on hydrochloric acid solutions. An evaporator and a membrane separator for hydrochloric acid recycle will be designed, built, and tested. Hydrochloric acid recycle apparatus will be installed and integrated into the plutonium facility operations. Present nitric acid waste solutions from plutonium processing contain both amounts and concentrations of nitrates far above desired levels to meet environmental objectives. Potential leaching of soluble salts (nitrates and chlorides) from cemented radioactive wastes is an unknown which raises major concern. It is very desirable to reduce quantities of TRU wastes to a minimum. Acid recycle promises to provide significant relief in each of these areas.

Nitric acid recycle by evaporation and distillation has been used in uranium operations at Y-12. Savannah River Site has recovered and reconcentrated nitric acid as part of their operation. Pacific Northwest Laboratories has built pilot-scale apparatus for potential acid recycle use at Hanford. New Los Alamos work using freeze-drying for decontamination of nitric acid waste solutions could be integrated with this work.

Recycle of both nitric and hydrochloric acid presents no major technical risks. Evaporation and fractional distillation are both mature technologies. While these have not been applied to recycle of plutonium waste solutions as integrated processes, much industrial production of nitric and hydrochloric acids use this approach.

8. Expected Payoff:

Applicability: Aqueous processing of plutonium residues; cleanup of previous plutonium processing residues.

Benefits:

* Reduce construction cost of replacement waste handling facility by over $10M
* Major reduction in waste disposal costs
* Reduced number of waste units requiring handling, inspection, packaging, shipping, storage, etc.
* Acid reagent costs reduced
* Potentially leachable nitrates, chlorides in waste reduced

Capability: At least 95% of the acid will be recycled. Acid concentrations will be sufficient for reuse in processing.

Cost-savings example based upon analysis of previous Rocky Flats operations:

* Total salt-crete production reduction of 50%

* Waste disposal costs reduction of $12M/year
* Nitric acid reagent costs reduction of $100K/year

9. Milestones/Accomplishments:

1. Program start	12/94
2. Receive membrane separator	12/94
3. Receive HNO3 test column	02/95
4. Construct HCl test evaporator	03/95
5. Complete HCl test evaporator experiments	08/95
6. Complete HNO3 column tests	09/95
7. Interim report on HCl test evaporator	09/95
8. Interim report on HNO3 test evaporator	10/95
9. Complete membrane separator tests on HCl concentration	10/95
10. Interim report on HCl membrane separator tests	11/95
11. Complete conceptual design of full-scale HCl recycle system	12/95
12. Evaluate feasibility/efficiency of membrane unit	03/96
13. Complete bench-scale testing of crystallizer concept	04/96
14. Complete design of "hot" 2-stage HCl evaporator	06/96
15. Interim report on HCl "cold testing"	06/96
16. Complete construction of "hot" HCl evaporator	09/96
17. Report on HCl recycle concept tests and apparatus design	09/96

The HCI test system has been installed in a hood in a "cold" lab. System controls and sensors have been wired to a computer control. Software has been written for data acquisition/control for the system, and tests of all controls are underway. Initial evaporation experiments will start shortly. The glass HNO3 test column has been assembled in a "cold" lab, and ventilation modification will permit test operations soon. GPP funding was obtained from DOE for the design, construction and installation of the full-scale HNO3 distillation column.

10. Transition Plan:

Following successful demonstration of acid recycle, acid recycle will be applied to all acid wastes from the Plutonium Facility at Los Alamos. Previous nitric acid effluent solutions have amounted to 75,000 L/year. Hydrochloric acid processing has had limited prior use, but future use may be at 15,000-25,000 L/year level. Both performer and user are the same. No industrial participation is foreseen.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	258	169	200	280	907
DOE	0	0	188	200	300	688
TOTAL	0	258	169	200	280	1,595

12. Performers:

Department/Agency Laboratory: Los Alamos National Laboratory will conduct the work.

Industry involvement: No industrial involvement is foreseen at present.

Planned cooperative development agreements: There are no planned cooperative development agreements

13. Principal Investigator:

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14. Keywords:

Recycle, Reconcentrate, Acid, Plutonium, Nitric Acid, Hydrochloric Acid, Effluent

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Recycle Boiler Nitrite Solution

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Facilities Engineering Service Center (NFESC)

5. **Project ID:** #69

6. **Problem Statement:**

The nitrite solutions used for marine boiler tube hydroblast, lay-up, hydrostatic testing, and rinsing must be recycled to the extent possible and then treated for NPDES disposal with minimal nitrate conversion. The Navy uses nitrite extensively as a rust-preventing fluid in marine boiler maintenance. Because it oxidizes readily to nitrate, it will support surface water eutrophication and is therefore treated as a "de facto" hazardous waste regardless of whether contaminants are taken up in its usage. This has resulted in high disposal costs.

NFESC has been working on this problem since FY90 and has developed a highly successful treatment process, based on sulfamic acid, that converts nitrite to nitrogen gas with little or no conversion of the nitrite to nitrate being caused by the treatment itself. Working with the Naval Station, Treasure Island, CA, it has been determined that the nitrite solutions can be recycled a number of times as long as they are stored under an oxygen free head gas and are treated and disposed of before the nitrate concentrations acquired from hydroblasting, lay-up or hydrostatic testing do not reach unacceptable levels. The challenge now is one of bringing these technical requirements into a cost-effective and dockside acceptable system that will eliminate the need for exporting nitrite wastewater.

This is an enhancement to an on-going 6.3 technology demonstration project. It addresses SERDP Thrust 3.A.2.b: Metal working Process/Cleaning & Degreasing, and it supports a SERDP goal to minimize or eliminate hazardous wastes at the source.

7. **Project Description:**

The goal of this project will aim at: (1) full scale design and demonstration testing of the sulfamic acid process at a selected Naval activity; (2) designing an oxygen-exclusive, conditioning process for bringing the used nitrite solutions back to specification quality; and (3) development of a practical procedure for long-term storage of recyclable nitrite solutions without head-gas caused nitrate formation.

Full scale sulfamic acid process demonstration will be accomplished at the Naval Air Station, North Island, San Diego CA, the NFESC plant that was successfully tested in FY92. This will

be an operational demonstration using Naval personnel and nitrite wastewater solutions from ship(s) being serviced there. Samples will be taken to fully characterize the wastewater before and after denitrification process. These data will be used to determine the processing necessary to restore the liquid to specification quality. Previous data obtained by NFESC show that reconstitution should be quite practical. A system will then be designed, fabricated, and tested. The final process step will be the design of a system that will permit the oxygen-free storage of the reworked nitrite solution. Operating procedures will then be defined that will govern the use of the nitrite solution in a manner that will ensure extended cycles of service.

The technical risk is very low. The project addresses Tri-Service Environmental R&D Strategic Plan, Requirement (I.2.b): Non-polluting, Non-toxic Cleaning and Degreasing Technology.

8. Expected Payoff:

Take Long Beach Naval Shipyard as an example, the average cost of disposing of the approximately 500,000 gallons of nitrite wastewater generated annually is about $1,500,000 at $3.00/gallon.

After successfully implementing the NFESC hydroblast recycling process, it has been estimated that the total volume of sodium nitrite wastewater generated by all Naval shipyards to still be about 3 million gallons each year, and by Navy-wide boiler maintenance operations to be 10 million gallons per year. The proposed chemical denitrification process has the potential of reducing the disposal cost by at least 95 percent (reduced from $3.00/gallon to $0.15/gallon operating cost) or $8M savings per year for Naval shipyards and $17M savings per year for the Navy-wide boiler maintenance operations.

The proposed chemical process will not produce hazardous waste and the effluent produced can be safely discharged to the sanitary sewer.

This project should have very high transition opportunities because of the high payoffs.

9. Milestones/Accomplishments:

1. Program Start	10/94
2. Complete Nitrite Solution recycle/storage evaluation	10/95
3. Complete System design of Denitrification Process	02/96
4. Complete test and evaluation plan and permit application at test site	02/96
5. Complete full scale demonstration	07/96
6.Complete development of User Data Package and final reports	09/96

A 5,000 gallon capacity centralized full-scale denitrification process has been designed as an integral part of Industrial Wastewater Treatment Plant (IWTP) at NAS North Island, CA.

10. Transition Plan:

At the conclusion of this project, the proven full-scale demonstrated system will be left at the host site for continuous operation. Implementation throughout the Navy will be done through the cooperation with Naval Ship Systems Engineering Station (NAVSSES). The technology transfer documentation (User Data Package) will be published as a final deliverable. This UDP will contain information on system design & specification, O&M, permitting, training, and safety plan. The other DoD agencies and private industry will have access to the information developed and, with it, will be able to apply the technology thus described as desired.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	475	68	200	743

12. Performers:

NAVY/NAVSEA/NFESC and EPA. The Risk Reduction Engineering Laboratory of EPA, Cincinnati, will team with NFESC on this effort and has proposed to the SERDP Executive Director the evaluation of a biological system that will convert both nitrite and nitrate to nitrogen gas.

13. Principal Investigator:

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14. Keywords:

Nitrite, Nitrate, Denitrification, Sulfamic Acid, Nitrogen Gas, Boiler

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Utilization of Biomass Technologies on Military Installations

3. **Agency:** U.S. Environmental Protection Agency (EPA)

4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)

5. **Project ID:** #227

6. **Problem Statement:**

The goal of this project is to determine the technical, economical, and environmental feasibility of small innovative energy conversion technologies fueled with biomass. The DoD, and numerous other institutions, operates a large number of small energy conversion systems that burn fossil fuels and are in need of repair or replacement. These systems emit substantial amounts of air pollutants (SO_2 and particulate) which must be controlled. Installing biomass fueled systems or converting or replacing existing equipment with systems that utilize biomass would eliminate SO_2 emissions, produce zero net gain of CO_2 emissions, reduce air toxic emissions, and reduce waste disposal problems. The objective of this project is to demonstrate, test, and evaluate a biomass fueled innovative energy conversion technology at a DoD installation. The research category for this project is applied research, and technology demonstration and technology transfer. This project is an enhancement to the previously SERDP funded (FY93) project and continues to be an opportunity for the DoD, EPA, DOE, USDA, AID, national labs, and industry to cooperate in demonstrations that will benefit each organization.

7. **Project Description:**

The technical objective of this project is to demonstrate that small innovative energy conversion technologies fueled with biomass are technically, economically, and environmentally feasible for DoD installations, industries, and developing countries. Existing efforts have focused on large scale systems or mature technologies. The small scale innovative energy conversion technologies have been neglected. The technical approach for this project is to identify interested DoD sites (many military installations have expressed interest and two have offered to be a host site), identify the project cooperators, select the most viable technology, and design, build, and test the system. The coordination between DoD and cooperators would be such that the design of the project would be in the best interest of the host DoD installation. The biomass fuel supply would be generated by activities on-site, in the community, and/or from dedicated feedstock supply systems (DFSS). The technical risks would be minimized by the proper selection of technology based on the available site, size of system, type of fuel, qualifications of operators, and lessons learned by all cooperators. The project would build upon the EPA/OPPE and DoD study "Enhancing Management of Forests and Vegetation on Department of Defense Lands: Opportunities, Benefits, and Feasibility;" the EPA/NRMRL, Southeast and Southwest Regional

Biomass Energy Programs, and DOE funded Sutton/ENERGEO and Cratech biomass-to-energy projects; the EPA/NRMRL, DOE, and AID biomass integrated gasification/gas turbine study; the EPA/NRMRL multi-fuel combustor research; the EPRI Distributed Generation Study; the USDA work with a wood fired combustion turbine, utilization of wood pallets and marketing of cull trees; the NREL gasifier scale-up in Hawaii; the Western Research Institute work with co-firing wood and coal in a turbine; the Regional Biomass Program for utilization of biomass; and ORNL research in DFSS. The project relates to the needs of the DoD by supporting Pillar 3 of the Tri-Service Research Plan, Thrust 3.M: Reduce greenhouse gas emissions, (3.V.2.d) Improve efficiencies of mechanical systems and (3.V.3.a) Alternative/renewable energy sources and the DOE by supporting Title XII: Renewable Energy of Energy Policy Act of 1992, H.R. 776/Public Law 102-486, direct combustion or gasification of biomass and biofuels energy systems.

8. Expected Payoff:

After successful demonstrations, energy conversion technologies fueled with biomass could be applied in developed or developing countries, industrial sites, rural areas, as well as, DoD installations. The technologies could be modularized to allow for varying fuel supplies, energy demand, and transportability. The benefits for the DoD to install biomass fueled systems are 1) reduce air emissions, 2) minimize on-site and community biomass waste disposal, 3) savings from tipping fees, purchase of fossil fuels, and electricity, 4) energy security at domestic and international military installations, and 5) promotion of exportable technologies.

9. Milestones/Accomplishments:

1. Identify host site(s), existing systems, fuel supply	08/93
2. Cut-off date for Preproposals under solicitation	12/93
3. Preproposal evaluations completed	02/94
4. Final application due to EPA Grants	03/94
5. Award of Competitive Cooperative Agreement	07/94
6. Identify site/existing utilities, characterize fuel	10/94
7. Interview technologies	10/94
8. Select developer	01/95
9. Contract and begin design	03/95
10. Begin site preparation & construction	06/95
11. Complete designs and equipment selections	01/96
12. Deliver initial equipment module to site	06/96
13. Complete plant installation & shakedown	08/96
14. Planned completion date	07/97

Solicited project preproposals were received and evaluated; Research Triangle Institute (RTI) was selected with cooperation from the North Carolina Department of Commerce's Energy Division and USMC Base Camp Lejeune. EPA Grants awarded a Competitive Cooperative Agreement to RTI. A MOU was signed between EPA and Camp Lejeune and A MOU was signed between RTI and the State of North Carolina. Briefings have been given to Camp Lejeune's CG Livingston, Col. Randall, and Col. Clemmer. Planning meetings have been held with Base facilities,

environmental, and forestry departments. Lejeune selected more than five potential demonstration sites and performed studies (traffic, existing utilities, existing infrastructure, effects on base facilities budget, groundwater, environmental, aesthetics) to select the best site. Timber cutting and clearing of the site have been completed. Site utilities estimates have been performed. Building design has been completed and ordered. RTI issued a RFP from equipment developers. Equipment developer's proposals were received and evaluated. EPA and RTI inspected 5 potential technologies (ENERGEO, Inc., Thermal Technologies Inc.(TTI)/Mech-Chem Associates, Inc., Cratech Inc., Thermogenics, Inc., and Power Generating Inc.). TTI/Mech-Chem was selected and contracted with to provide the technology to be demonstrated. RTI/TTI/Mech-Chem/EPA/Ellicottville Energy performed system test runs with Ellicottville's system. System engineering reviews have been performed and release of drawings for equipment fabrication and installation has begun. Fuel samples have been analyzed. Fuel drying/feed system has been designed, equipment ordered, and some deliveries received. NC Energy Division contracted with International Applied Engineering, Inc. to provide engineering services (system evaluation support). A NC state air quality permit has been issued.

Emerging Small Systems for Power Generation from Biomass was presented at the First North American Conference & Exhibition: Emerging Clean Air Technologies and Business Opportunities Conference in Toronto, Canada. Demonstration of a Small Biomass Power Plant, Development of a Small Scale BIGGT Power Plant, and Demonstration of a 200-Kilowatt Biomass Fueled Power Plant were presented at the Sixth National Bioenergy Conference in Reno, NV. Emission Control of Small Fluidized Bed Combustors Utilizing Biomass Fuels was presented at the Pacific Rim International Conference on Environmental Control of Combustion Processes in Maui, HI. Wood Waste from Marine Base to Generate Electricity press release was issued. Installation of an ENERGEO Biomass Power Plant at a Lumber Company was presented at the 1995 Greenhouse Gas Symposium in Washington, DC. Demonstration of a 1 MWe Biomass Power Plant, and Development of a New Generation of Small Scale Biomass-Fueled Electric Generating Power Plants were presented at the 1995 Greenhouse Gas Symposium in Washington, DC and at the Second Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry Conference in Portland, OR. Independent Power Plant Using Wood Waste was presented at the Greenhouse Gases: Mitigation Options Conference in London, UK.

10. Transition Plan:

This project would provide the jump start needed for the development of equipment, design of systems, creation of new markets, and realization of existing untapped markets for biomass fueled energy conversion systems. The potential systems will be comprised of off-the-shelf components or components manufacturable by existing industries. A successful demonstration would allow developing countries to get approval for financing from multi-lateral lenders. Developing countries are in dire need of this type of technology because biomass waste is both a disposal and air pollution (open burning) problem and diesel fuel is too costly to import. Biomass fueled technologies will help provide sustainable energy without being detrimental to the environment.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	750	920	580	550	2,800

12. Performers:

The amount of government/industry cooperation required for a project of this type should lead to future CRADA's between government and industry. Demonstration of an energy conversion technology utilizing biomass will be performed through the cooperation of the EPA, DoD, DOE, USDA, AID, national labs, and industries. The EPA/NRMRL, the lead organization, has a cooperative agreement with Research Triangle Institute (RTI). With DoD assistance, EPA/NRMRL evaluated preproposals and requested RTI to submit an Application Kit to EPA/GAD. A management task force has been formed with representation from EPA/AEERL, RTI, NC Energy Division, and Camp Lejeune. EPA/NRMRL and RTI, with assistance from the task force, has selected the technology developer, Thermal Technologies, Inc. and Mech-Chem Associates, Inc. EPA/NRMRL and RTI, with assistance from the task force will proceed with evaluation of environmental and site specific data, and coordinate project participant's activities. TTI/Mech-Chem is providing the system development/design and hardware. The NC Energy Division has entered into a $100K contract with International Applied Engineering to support the project. Camp Lejeune will provide the demonstration site, specific information to aid the technology selection process, and possibly system operators. Sandia National Lab will be asked to assist with instrumentation, data collection and analysis, etc. DOE's Office of Solar Energy Conversion/Solar Thermal and Biomass Power will be asked to cofund the project. SERBEP, USDA, NREL, and ORNL will provide off-site resource information, including DFSS. AID/Winrock will be asked to examine opportunities for transferring technology to international markets.

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14. Keywords:

Biomass-to-Energy, Energy Conversion, Combustion, Gasification, Gas Turbine, Distributed Power Generation

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Integrated Expert Solvent Substitution Data Base

3. **Agency:** U.S. Environmental Protection Agency (EPA)

4. **Laboratory:** HQ and Air and Energy Engineering Research Laboratory (AEERL)

5. **Project ID:** #331

6. **Problem Statement:**

The goal of this project is to build an integrated solvents substitutes umbrella or architecture which will link and draw from existing data bases and data sets in each of the participating and other agencies. This architecture will be built as a component of a larger federal P2 electronic information resource platform known as Enviroene. The resultant expert tool would combine priority information from each existing data base such as compatibilities and performance, and fill gaps by providing economic analyses and vendor information. It would be targeted for direct use by all DoD depots, logistics centers, defense contractors, small and medium industries as well as State Technical assistance offices, NIST Manufacturing and Technology Centers, and university industrial service programs. This data base could provide an important technology transfer function for Federal Agencies, states, and small and medium industries to advance the implementation of P2 technologies and alternatives and the reduction of hazardous waste releases/emissions in meeting the Executive Order on Federal Compliance's (12856) 50% reduction of TRI toxics by 1999, and the Clean Air Act/SNAP hammer deadlines. It will assist in the redevelopment of many Mil Spec Standards under executive Order 12856, and will assist each agency and the US in meeting its ozone depletion reduction, and toxics use reduction goals. The data system will also assist DoD in implementing P2 projects through the ENNVEST program under the President's Regulatory Reinvention Initiative. The project will also demonstrate federal cooperation and environmental leadership by promoting and making publicly available the successes and lessons learned by the participating agencies.

7. **Project Description:**

Develop an integrated expert solvent substitutes data base that will combine related data base efforts across agencies and expand those efforts in depth and breadth. Objectives would include targeting related solvent data base tools for integration; develop Enviroene Web platform; develop expert architecture with component engines and decision trees; convert and integrate phase 1 component data bases; modify architecture per user feedback; integrate phase 2 component data bases; conduct continuous data set update; conduct deployment/feedback program.

This project promotes the SERDP objective of maximum exchange of information via several deployment mechanisms. It is designed to assist government agencies and industry as an information exchange data base to be linked with the Enviroene, DENIX, EPIC, and TECNET networks over INTERNET for widespread electronic access. This array of electronic dissemination of DoD and DOE solvent alternatives knowledge and leadership meets a second objective of SERDP, to provide appropriate access (to federal, state, and local governments and industry) to data available to DoD and DOE relevant to environmental matters. The National Center for Manufacturing Sciences and the National Pollution Prevention Roundtable Programs are committed to networking the final product throughout their membership. The Roundtable, and NIST MTC's, represent a massive hands-on deployment mechanism. More than 70 technical assistance centers operated by these programs will use the tool in on-site assessment visits to industries within their jurisdictions.

This project implements a third objective of SERDP by minimizing the duplication of environmentally related research. The purpose of this project is to integrate similar solvent substitute data bases and focus on growth of the integrated tool through a coordinated, monitored effort by representatives of a technical review board. This project will integrate information on alternatives from a number of existing test centers. We intend to access information from the DOE National Laboratories; DoD's National Defense Center for Environmental Excellence (NDCEE); and the Illinois Hazardous Waste Resource Information Center. Other validation test bed facilities will be considered for inclusion.

This project meets a fourth objective of SERDP, by spurring three tiers of development and demonstration activities. These three tiers include research and development to design a system architecture for component data base tools; the development of an expansion strategy that will operate a testing regime to generate new data for the integrated data base; and the implementation of an update program which will use existing test bed centers as information sources.

By deploying this expert data base through the depots and logistics centers, national labs, State, NIST and EADS technical assistance centers we are providing governmental and nongovernmental entities with analytical assistance in reducing toxics use and meeting the bans of ozone depleting substances under the Clean Air Act the Montreal Protocol, and Executive Order 12856. We are therefore meeting a fifth objective of SERDP, providing analytical assistance in reducing military and industrial ODS impact on the stratospheric ozone layer. This objective will be met by networking this expert tool throughout all service bases and joint depot maintenance shops. More massive impacts will be seen with widespread application of the tool to the small and medium businesses of the plating, fabrication, electronics and maintenance and repair industries.

The project will build on the EPA's Solvent Alternatives Guide (SAGE), and PIES Vendor data bases; DOE/INEL's HSSDS and SHSD databases; the National Center for Manufacturing Sciences (NCMS) Solvent and Materials Compatibility data bases; and others as identified. Ultimately the system will be comprised of a fully integrated data base that builds on aspects of SAGE to assist users in identifying alternative technologies and chemical groups based on their

knowledge of the application. The system will be supported by compatibility and chemical test data (from INEL HSSDS, SHSD, and NCMS) to assist users in identifying suitable replacement chemicals/technologies for their application; vendor information (from PIES and NCMS) to identify sources for alternatives; and case study information (from PIES) to provide information on effectiveness, payback and potential problems with the alternative selected. The data base developed under this project will focus exclusively on solvents and will serve as a model for subsequent expansion efforts to address other industrial sector applications.

The project will enhance the technology transfer work of the PIES expansion project, now known as Enviroene, under SERDP in 1993 where information umbrellas are established within the P2 network, as well as on the GUI programming research initiated under that project.

Project Tasks: The tasks involved in this project encompass:
1. Establish a Technical Advisory Board/User group: This board, representing participating Agencies and targeted users, will guide each stage of this project. It will set the priorities in the testing and validation phases, design requirements of the final system, and beta test various project accomplishments.
2. Identify information sources and relationships: This task will involve an exhaustive search to identify other data bases that should be considered in the integration. This task will evaluate: function; data gaps; relationships between data bases; areas of duplication; and data formats and file structures.
3. Expand the Enviroene information umbrella: This builds on FY93 SERDP funding which establishes information umbrellas pointing to several tools under a single network. These will be expanded to house other solvent systems from federal and private sectors.
4. Develop system Phase I architecture to integrate component tools: Component systems will be integrated and combined in two phases (phase one data bases will be addressed in 1996 and phase two will be addressed in 1997). Phase I efforts will include development of the Environene Web support platform, as well as component decision trees and search engines. This effort will provide a seamless, integrated data environment and enable the user to navigate easily through several tools without the need to learn separate operating command structures.
5. Refine network, architecture, engines and tools accessed per user feedback: Phase 1 and 2 platforms and umbrella architecture will be field tested and modified per user feedback to improve accessibility, functionality and ease of use.
6. Develop system Phase 2 architecture: Phase 2 data bases will be converted and integrated into the umbrella. Expanded decision trees for primary users groups will be implemented.
7. Update technical data sets: New information will be added to the component data sets and data bases from test bed centers at the DOE National Laboratories, Academic test bed centers such as the Illinois Hazardous Waste Resource Information Center and the NDCEE.
8. Deployment/marketing/training: The system will be deployed to DoD and the tri-services targeting the depot and logistics centers using hands-on training workshops. In addition State Technical Assistance Programs, NIST MTC's and the Regional Centers of the National Pollution Prevention Roundtable will participate in the training and outreach efforts for industry, and by relaying the use of the system in their on-site industrial assessment programs. EPA and States will directly network with local Chambers of Commerce. In addition, INTERNET itself will be used to increase exposure and ease access to Environene and the solvent alternatives umbrella

through linkages to various locators and search services including the Thomas Registry of American Industry, other technical assistance sites such as the NASA Technology Transfer Network and others. EPA will also explore the potential for embedded bookmark linkages within common Internet navigators such as Netscape.

8. Expected Payoff:

The benefits of this effort for DoD, DOE, and EPA include better centralized access to pertinent information to reduce the use of toxic and ozone depleting solvents; this access will help federal agencies meet the phase outs under the CAA and numerous executive orders; Environene will assist DoD in establishing P2 projects under ENNVESTR which will be used as alternatives to typical environmental compliance, providing superior environmental benefit and compliance cost savings; a reduction of redundant information collection, research, and testing efforts. In addition, Enviroene will reduce Federal expenditures for document printing and travel related to outreach and environmental training. The benefits to industry include easier access to technical information that will allow them to implement alternatives and reduce the emissions of ODS and other toxics; and assist in meeting the bans under the Clean Air Act. Industrial benefits include monetary savings and liability reduction due to implementing P2 alternatives. The project will provide a measurable indicator of its impact on industrial facilities in terms of cost savings and ODS reduction gained through options implemented.

9. Milestones\Accomplishments:

1. Establish technical advisory board	09/94
2. Complete architecture requirements analysis	11/95
3. Link case study data base into umbrella	11/95
4. Conduct training workshop	11/95
5. Establish quad web support platform - triad of support sites operational 1/96	ongoing
6. Complete phase I data base conversion and add to ISSDS (7 db's integrated as of 1/96)	ongoing
7. Develop Web communication function (interactive form capability added 11/95)	ongoing
8. Link SHDS data base into umbrella	01/96
9. Complete phase I decision tree	ongoing
10. Complete and link integrated vendor data base into ISSDS vendor info and DLA green guide added 1/96	ongoing
11. Activate phase 1 expert architecture prototype	01/96
final phase 1	05/96
12. Add 1st test bed center update of new info to HSSDS	06/96
13. Conduct additional training modules for DoD tri-services	06/96
14. Complete relational reporting function	07/97
15. Link regulatory guidance umbrella to ES	09/96
16. Complete field evaluation of phase I architecture	10/96
17. Complete phase I source characterization and data collection for ISDDS expansion	12/96
18. Complete evaluation of other DoD data bases	12/96

19. Modify based on feedback: Phase 1 platform, architecture, decision trees, and search engines 12/97
20. Complete conversion and linkage of phase 2 ISSDS data base 08/97
21. Modify based on feedback: Phase 2 platform, architecture, decision trees and search engines 12/97

Major accomplishments to date include bringing the Enviroene web and BBS platforms on-line and available to the public with more than 3,000 data files exclusive of component data bases and more than 16,000 data files inclusive of component data sets. The DOE EPIC information system was established as a sister system for DOE P2 and energy conservation information. Initial progress on the Solvent Alternatives Umbrella allows 7 component data bases to be searched simultaneously and a prototype decision tree architecture is now being tested. Five DoD data bases are now available through Enviroene. The Enviroene Web platform has been linked to other DoD sites, including DENIX, NDCEE, and NCTAMS. The initial training workshop template was developed and tested in two workshops conducted for participants from 7 Navy and Marine installations. The workshop conveyed internet navigation and resource training as well as technical information on ODS, solvent alternatives, painting/depainting, VOCs and electroplating. Participant feedback was very positive and indicated that deployment should be expanded and that the system already assisted participants in the writing of their pollution prevention plans. Tracking statistics already showing DoD as a primary user of the system. Estimated printing cost savings have already been estimated at $500K to $750K per year.

Other accomplishments include implementation of a number of tools to assist industry in identifying P2 options, including industry content guides; industry sector notebooks; linkages to industrial sites like 3M, Texaco, NCMS, NMEN, the Thomas Register and others to enhance access to alternative product information; the development of a subhome page for the American Institute for Pollution Prevention as a part of Enviroene; and linkages to the Business Advisor developed by the National Performance Review to assist small businesses.

10. Transition Plan:

The expert system will be accessed by industrial users directly through Internet. Also, the State TAPs, NIST MTCs, and the universities implementing DOE's EADS Program, will network the system through their on-site P2 assessment visits. Industrial access will also be gained through a direct networking/training effort for local Chambers of Commerce and Trade Associations. Direct deployment to DoD will occur through numerous tri-service training workshops dedicated to conducting Internet and Enviroene resource training and use; search engine training and use; and specific topical technical analyses based on pre-surveys related to ODS, painting/depainting, solvent alternatives, etc.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	3,000	0	1,000	1,000	5,000

12. Performers:

DoD: Navy: Naval Facilities Engineering Service Center, Larry Hill. DOE: ER Arnold Edleman. INEL: Kevin Twitchel. EPA: AEERL, Charles Darvin. Nat. Cent. for Man. Sciences, Len Stenger. WRRC: Vic Young. U. Wisc. Solid & Haz. Waste Ed. Center, David Lieble. IL Haz Waste Res. Info. Center, Gary Miller. Nat. Pol. Prev. Roundtable, Natalie Roy. SAIC, Michelle Passerelli. RTI, Ken Monroe.

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14. Keywords:

Solvent, Network, ODS, P2, Compatibility, Vendors, Substitute, Alternatives

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Trapped Vortex Combuster for Gas Turbine Engines

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory

5. **Project ID:** #1042

6. **Problem Statement:**

This year the EPA is expected to adopt the recommended aircraft engine emissions regulations made by the International Civil Aviation Organization (ICAO). These regulations are expected to decrease Nox emissions to (32+ 1.6*PR) g/ kN thrust, where PR is engine overall pressure ratio. The unburned hydrocarbons (UHCs) and carbon monoxide (CO) are expected to remain constant at 19.6 g/kN thrust and 118 g/kN thrust respectively. Although military aircraft are expected to be exempt from the regulation, there is a long standing policy (Attachment 3 of Air Force Regulation 19-1) that simply says that the Air Force will make a best effort to comply with EPA aircraft emission regulations while maintaining the high performance needed to ensure flight safety and combat superiority. The Navy has a similar policy as applied to land and marine (L&M) gas turbine engines for electrical power generation and their compliance with applicable federal and state emissions regulations.

Another real concern is that several states have regions that are in noncompliance with the Clean Air Act Amendments and their attempts to bring those areas back into compliance could hinder military operations. In California a State Implementation Plan (SIP) was developed to follow the Federal Implementation Plan (FIP) which placed caps on emissions of NOx, VOCs, and PM-10 in local regions. The caps apply to military bases located in the noncompliance regions, however, the cap does not include military aircraft emissions. The caps include aircraft ground support equipment (AGE) and other mobile and stationary sources of air pollution. The FIP emissions cap does affect ships operating at Naval bases and along the California coast. Specifically, shipboard gas turbine engines used to generate electrical power do not conform with the anticipated regulations. In a display at the First Annual SERDP Symposium, Dr H. B. Urbach of the Carderock Division Naval Surface Warfare Center made note of the following: "The Naval commands operating within the California littoral have been directed to make a good-faith attempt to comply with anticipated state and federal limits on NOx emissions." Although emissions from aircraft and L&M power generation gas turbine engines are of concern to both the Air Force and the Navy, the magnitude of the problem has not been fully appreciated. A study was conducted by the Combustion Branch at Wright Laboratory in an attempt to quantify the magnitude of pollutant emissions from Air Force and Navy air operations. The study was limited to the emissions of the C-5, C-141, B-52, KC-10, F-15, F-14 and F-18, and on Minot

AFB, Dover AFB, Seymore-Johnson AFB and Naval Air Station (NAS) Lemoore. Currently all military aircraft meet the NOx requirement, but our fighter aircraft are within 5% of that requirement. ICAO is already considering another 16% decrease in NOx emissions. If this change were to occur, many current fighters and next generation fighters designed around current technology engines will not meet the NOx emissions requirement. Many of the aircraft in the study, the B-52H, C-141, C-5, KC-10, F-14, F-18 do not meet current UHC regulations. The B-52, F-14 and F-18 do not meet CO regulations and the F-15, C-141, and KC-10 are within 5% of the current regulation.

The magnitude of air base air operations pollution is just as substantial. Minot AFB (B-52H) currently produces over 1000 tons of UHC and 1000 tons of CO per year from their aircraft operations. This is more than 10 times that produced by all of the air operations at LAX, one of the busiest and most heavily regulated airports in the nation. Seymore-Johnson AFB (F-15) and NAS Lemoore (F-14) each produce over 1000 tons of NOx a year from their aircraft operations alone. This is nearly 10 times that of LAX. A comprehensive survey of all military aircraft and military bases is currently being conducted to quantify the true magnitude of this problem.

This project will demonstrate a revolutionary trapped vortex (TV) combustor concept for reducing emissions in military aircraft and land and marine (L&M) based electrical power generation gas turbine engines. The objectives of this project are to develop an optimized trapped vortex design for use in the General Electric IHPTET Phase III prototype gas turbine engine and to evaluate the use of a trapped vortex combustor for reducing NOx emissions in stationary gas turbine engines used on-board Naval vessels for power generation.

7. Project Description:

The goals of this project are to demonstrate the feasibility of developing a Trapped Vortex (TV) combustor that will: 1) reduce aircraft pollutant emissions (NOx, VOCs, CO, and PM-10) by 60%, bringing them significantly below the proposed 1996 EPA regulations, and 2) reduce NOx emissions by 60%, bringing them below the 1995 EPA regulation for L&M based gas turbine engines burning distillate fuels and 3) decrease specific fuel consumption by 3% (SFC, fuel mass flow rate required to generate a unit of thrust).

There are several significant differences between the operation of a TV combustor and a conventional combustor as well as the obvious difference in mechanical complexity. The first is that the TV combustor has a premixed flame in the main combustion chamber, whereas, in a conventional combustor fuel and air are injected separately into the combustion chamber and burn while being mixed. The second difference is that the TV pilot flame maintains its stability because the recirculation zone or vortex is contained in a cavity which protects it from main air flow, versus conventional combustor that stabilize the flame aerodynamically in the main flow field. Third, the TV pilot flame has a separate source of fuel and air that can be tailored to the mission of the engine. The primary zone in a conventional combustor cannot be so easily controlled. Fourth, the stability of the TV pilot flame allows the combustor to operate with high inlet velocity. Fifth, the blockage in the diffuser and the combustor are low. Thus, the pressure

drop across the combustor/diffuser system is low. These differences between TV and conventional combustors have important ramifications for emissions, fuel efficiency, weight, cost, and performance.

There are many technical issues that must be overcome before the TV concept can be tested in an engine. A new diffuser between the compressor discharge and combustor inlet must be designed. The diffuser will also be where the fuel is injected and mixed so a new injection/mixing scheme must be developed and incorporated into it. The combustor section including the trapped vortex concept must be designed and tested. Finally a thermal management system to cool the diffuser, combustor and turbine inlet must be developed to handle increased thermal loading associated with increased performance. General Electric in conjunction with the IHPTET program will handle the Diffuser and Thermal management design and testing and Wright Laboratory will work in conjunction with them to design and incorporate the low emissions TV combustor with their design efforts. There are several issues associated with the optimum design of the TV combustor. These center around the proper design of the cavity geometry to trap and maintain a vortex over a variety of flow settings, the injection of fuel and air into the cavity to maintain a flame, and the effect of residual swirl from the compressor flame stability. Cavity geometry will be varied experimentally in a large scale test rig and computationally to optimize flame stability and minimize emissions over a broad spectrum of operating conditions. Different fuel and air injection system and their placement will also be tested with the intent of optimum cavity performance with minimum emissions. The mixing of the cavity fuel and air must be efficient and rapid to reduce the dynamic hot spots that produce the NOx. To help the mixing, the fuel and air injectors must be strategically located over a large area of the combustor. Advanced fuel injection, or platelet technology will be investigated as a means of producing injectors that distribute and rapidly mix the fuel and air in the TV cavity. This same technology will also be investigated in the diffuser/fuel injector system. The impact of inlet on flame stability and air and fuel mixing in the TV cavity will also be studied.

8. Expected Payoff:

There is a two fold benefit to this project, significantly reduced pollutant emissions and fuel conservation. The environmental objective is to reduce NOx, VOCs, CO, and PM-10 aircraft emissions to 60% below the proposed 1996 EPA aircraft emissions regulations and to reduce NOx emissions by 60% below the California Resource Board recommendation of 42 ppm for L&M based gas turbine engines burning distillate fuels. The environmental impact of only military aircraft using the TV combustor technology that meets the project goals will be enormous. For example, assume that all existing military aircraft had TV combustors. The VOCs for the Air Force and Naval bases will drop by a factor of 10 in some cases, approximately 900 tons per base. The NOx emissions will be reduced by 20% to 40%, or 200 to 400 tons per base, depending on the aircraft at the bases. This will permit flight operations and training to continue at current levels with reduced or even eliminated fines due to pollutant emissions from aircraft.

Decreasing pollutant emissions and fuel consumption will have a significant impact on the stratosphere. In the stratosphere the benefit of reduced pollutant emissions of CO, UHC and

NOx is realized along with a benefit due to fuel consumption. The greenhouse gasses H2O and CO are a byproduct of hydrocarbon fuel burning. Aircraft spend most of their time at high altitudes, thus a 3% reduction in total emissions will reduce global environmental changes due to NOx reduction of ozone in the stratosphere and the greenhouse effect of CO2 and H2O emitted from high flying aircraft.

DOD will experience a considerable savings due to fuel conservation from the lower fuel consumption expected with this combustor. DoD purchases four to six billion gallons of aviation fuel per year at a cost of about $0.75 per gallon. A 3% savings in fuel consumption will save $120 million. The long term cost savings are so large that a retrofit project will be easily justified with relative short term pay-back cost.

If commercial aircraft also had TV combustors, then the environmental and cost impact improves by a factor of 8, since in the US commercial aircraft uses about 88% of the jet fuel consumed annually.

9. Milestones/Accomplishments:

No.	Milestone	
1.	Start Date	01/10/96
2.	Determine Flow Conditions for IHPTET Aircraft TVC	02/01/96
3.	Select Aircraft TVC Configurations for Studies	03/01/96
4.	Design TVC #1	03/01/96
5.	Fabricate Aircraft TVC #1 Sector	04/01/96
6.	Fabricate Test Facility High Pressure Test Section	04/01/96
7.	Checkout Test of Facility and Aircraft TVC #1 Sector	06/01/96
8.	Test of Aircraft TVC #1 Sector	10/01/96
9.	CFD Studies of Aircraft TVC #1	01/01/97
10.	Transition TVC Design Information IHPTET Build No. 1	01/01/97
11.	Design Aircraft TVC #2	03/01/97
12.	Fabricate Aircraft TVC #2	05/01/97
13.	Test of Aircraft TVC #2	10/01/97
14.	CFD Studies of Aircraft TVC #2	01/01/98
15.	Transition TVC Design Information IHPTET Build No. 2	01/01/98
16.	Select LM TVC Configurations for Studies	02/01/98
17.	Design LM TVC #1 Sector	04/01/98
18.	Fabricate LM TVC # 1 Sector	06/01/98
19.	Test LM TVC #1 Sector	10/01/98
20.	CFD Studies LM TVC #1	01/99/99
21.	Design LM TVC #2 Sector	03/01/99
22.	Fabricate LM TVC # 2 Sector	05/01/99
23.	Test LM TVC #2 Sector	08/01/99
24.	CFD Studies LM TVC #2	08/01/99
25.	Transition LM TVC Design Rules to NAVSEA	10/01/99
26.	Final Report	10/01/99

10. Transition Plan:

Four transitions are planned for this program. The first transition will be to the IHPTET program and will occur at Milestone 5. The data obtained at Milestone 5 will enable GE to arrive at an optimum design for a full annular TV combustor that will have a high probably of successfully meeting IHPTET performance goals and the low emissions goals established on this SERDP project. The second transition is to JAST. Unfortunately, the JAST program is not sufficiently defined so that one can plan when the transition will occur. However, the method of transition is clear. The GE JAST office must be assured that a TV combustor offers improved performance at a low risk. They will then include the TV combustor in their JAST plan. Three Milestones (8,14, and 17) are given at which the GE JAST team will review the TVC results to determine if it satisfies the JAST criteria.

The third transition is to the Navy as noted in Milestone 12. The Navy will review the results obtained on the L&M TV combustor configurations and make a determination about the value of testing a TV combustor in their facilities. Assuming positive results, they will prepare a proposal for testing the L&M TV combustor at their Philadelphia LM2500 test facility. It is not clear what the opportunities for funding will be at that time but an Environmental Security Technology Certification Program (ESTCP) project seems to be appropriate. Wright Laboratory will act as a consultant on this program.

The fourth transition of the TV combustor is to commercial aircraft and could take place at Milestone 15. The transition will be up to GE but it will take place in a natural way. GE has a history of transitioning engines developed by DoD commercial aviation and L&M engines for electrical power generation. For example, the F101 engine developed for the B-1 bomber led to the development of the CFM56 class engines used in the B737 and A320 commercial aircraft, so transition of the TV combustor will follow an established process.

11. Funding: ($K):

	FY96	FY97	FY98	FY99	TOTAL
IHPTET	500	1,500	1,000	500	3,500
PE 62203F	300	300	300	300	1,200
SERDP	500	500	500	400	1,900
TOTAL	1,300	2,300	1,800	1,200	6,600

12. Performers:

This program will be directed by the Combustion Branch of Wright Laboratory's Aero Propulsion and Power Directorate, WL/POSC and Naval Air Systems Command NAVSEA Code 03x32. General Electric Aircraft at Evendale OH will perform the CFD model studies,

design and fabricate the TV combustors for rig tests, and assist in the experiments, and prepare the final report. Wright Laboratory and an on-site contractor will perform the rig tests and conduct laser diagnostic studies of the combustion process to aid in optimizing the designs. The SERDP funds will be split between GE and the on-site contractor. In-house Air Force funds will pay for the Air Force team and the facility operation cost. Dr. John Hartranft of NAVSEA Code 03x32 is the Navy contact and will serve as a Co-Principal Investigator on this program and will aid with all aspects of this project relating to the L&M TV combustor evaluations. He will be responsible for future engine test of an L&M TV combustor. We will work out the JAST transition as the program develops.

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14. Keywords:

Gas Turbine Engine, Combustor, Low Emissions, Pollution Prevention

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Alternative Electroplating Technology

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX)

5. **Project ID:** #71

6. **Problem Statement:**

To replace hazardous plating processes (chromium VI, cadmium, cyanide, etc.) currently used on Naval aircraft (A/C), weapon systems (WS) and ground support equipment (GSE). Chromium VI and Cadmium are heavy metal pollutants and carcinogens. Cyanide is hazardous to human health. The Clean Air Act Amendment (CAAA) of 1990 (Electrolytic Chromium National Emission Standard for Hazardous Air Pollution (NESHAP), etc.) as well as other EPA and state Departments of Environmental Resources regulations restrict the emissions from these processes. In addition, CNO directives require significant reductions in hazardous waste generation. Presently, these plating processes are used in production and Depot level maintenance operations. Therefore, in order to comply with these regulations while maintaining aircraft performance and operational readiness, alternative plating processes need to be developed and validated. This effort is covered under the Tri-Service Environmental Quality Strategic Plan; Pillar 3: Pollution Prevention, Requirement Thrust: 3.I.3.e Non-Hazardous Alternatives for Heavy Metal Constituents used in Plating and Finishing and is a continuation of an existing 6.2/6.3 effort.

7. **Project Description:**

Chromium VI plating and cadmium plating are common inorganic corrosion preventive coatings. Chromium VI plating is also used to build up worn components when they no longer meet tolerance levels. Cadmium plating is frequently used for fasteners and other very tight tolerance parts because of the dual qualities of lubricity at minimal thickness and superior sacrificial corrosion protection. Replacements for chromium VI and cadmium will require similar mechanical and performance properties over the full spectrum of applications for which they are currently used. Tin-zinc and zinc-nickel electroplating both offer potential to fulfill many of the requirements of Cadmium plating. These processes provide characteristics which would meet the majority of the corrosion resistance and some of the lubricity requirements of Cadmium plating. A joint Navy/industry effort will optimize and demonstrate this capability. Another alternative to Cadmium plating which has potential to fulfill many of these requirements is aluminum-manganese (Al-Mn) electroplating from a molten salt bath. This process differs from the traditional aqueous electrolytic plating bath. This process is electrolytically applied in molten

salts in the low 300F temperature range and provides characteristics very similar to those of cadmium which include remarkably similar post plating relief cycles to those of cadmium. Optimum Al-Mn concentrations, for Naval aircraft use, will be isolated through a test program which examines the varied choices of Al-Mn systems on test coupons of various materials and sizes. This program will simultaneously establish safe operating practices and procedures for operating this bath to ease the transition to a new and unfamiliar method of electroplating. This bath formulation will then be established as a full size prototype at a selected NADEP. Following full scale tests Al-Mn will be transitioned to the fleet through specification modification and design changes. In addition, ion vapor deposited (IVD) aluminum is another demonstrated alternative for certain applications that will be pursued for Navy use. Other alternatives to hexavalent chromium plating and cadmium plating that will be investigated include electroless nickel plating and trivalent chrome plating as well as alternative application techniques with non-chromium/cadmium materials (physical vapor deposition, spray casting, flame spray/high velocity oxygen fuel, etc.). Finally, cyanide strippers have been used to remove metallic coatings. Non-cyanide strippers will be evaluated based on an Air Force investigation.

8. Expected Payoff:

The elimination of chromium VI and cadmium plating significantly reduces the total amount of hazardous materials emitted from Navy operations. Elimination of chromium VI plating also eliminates the need for expensive emission control equipment required by CAAA and AQMD legislation (estimated at several $M per Depot Facility). Furthermore, these alternatives significantly reduce disposal costs of chromium VI and cadmium from Navy operations. This effort is in direct support of Navy and DOD hazardous waste minimization policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, WS and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to commercial airlines and automotive industries, equipment manufacturers, fastener manufacturers, etc.

9. Milestones/Accomplishments:

1. Evaluation of Al-Mn Molten Salt Bath Electroplating	09/95
2. Electroless Nickel Optimization/Demonstration	09/95
3. Evaluate Zinc/Nickel Electroplating	03/96
4. Evaluate Tin-Zinc Electroplating	03/96
5. Optimization of Al-Mn Molten Salt Electroplating	09/96
6. Implementation of Electroless Ni Electroplating	09/96
7. Service Demonstration of Zinc-Nickel Electroplating	09/96
8. Optimize Zinc-Nickel Electroplating	12/96
9. Optimize Tin-Zinc Electroplating	12/96
10. Service Demonstration of Tin-Zinc Electroplating	12/96
11. Initiate Spray Casting Investigation	06/97
12. Initiate Physical Vapor Deposition Evaluation	06/97
13. Initiate Flame Spray/HVOF Process evaluation	06/97

14. Implementation of Tin-Zinc Electroplating	09/97
15. Implementation of Al-Mn Electroplating	09/97
16. Investigate Non-Cyanide Metal Strippers	09/97
17. Implementation of Zinc-Nickel Electroplating	09/97
18. Optimize Spray Casting Process	09/98
19. Service Demonstration of Non-Cyanide Metal Strippers	09/98
20. Optimize Physical Vapor Deposition	12/98
21. Optimize/demonstrate Flame Spray/HVOF Processes	12/98
22. Implement Non-Cyanide Metal Strippers	09/99
23. Service demo/transition Spray Casting Process	09/99
24. Physical Vapor Deposition Service Demo/Transition	09/99
25. Implementation of Flame Spray/HVOF Processes	09/99

The evaluation phase of the zinc/nickel and tin/zinc coatings is presently ongoing with corrosion and fatigue testing underway. There are yet to be fasteners coated with any of these coatings in order to perform torque-tension testing.

BIRL is doing a great deal of development work with the Al-Mn molten salt bath aimed at establishing the optimal processing parameters for the 10 gallon as well as the 200-300 gallon processing tanks. BIRL has identified 4 critical variables that must be controlled in order to provide a coating having the desired properties.

Electroless nickel has been implemented in this facility and we have accumulated significant service experience with this coating plated onto both steel and stainless steel substrates. It is a certainty that the coating has useful engineering properties and should be used where these properties are best exploited; however, it is equally certain that the electroless nickel should not be used as a general one-for-one substitute for hard chromium. It is suggested that the electroless nickel evaluation/implementation phase of the program be redirected to evaluate/implement electroless nickel and other coatings as hard chromium replacements.

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through coordination with the Lead Maintenance Technology Center for Environment. These processes will then be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials will insure availability for implementation.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	360	248	303	400	1,311

12. Performers:

Evaluation/demonstration of Chromium VI and Cadmium Plating alternatives is being performed by the Naval Air Warfare Center Aircraft Division Patuxent River, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. The Cadmium replacement efforts (Zn-Ni & Sn-Zn) also have Boeing, Peter Gumm and McGean Rhoco as industry partners. This effort is being coordinated with the Air Force (Tinker ALC, Tyndall AFCESA), the Army and aerospace industries (Boeing, Grumann, MDA-E, etc.).

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14. Keywords:

Electroplating Processes, Materials Substitution, Chromium VI Replacement, Cadmium Replacement, Alternative Plating Technologies, Non-Cyanide Processes

SERDP FY96 PROJECT

1. SERDP Thrust Area: Pollution Prevention

2. Title: Solid State Metal Cleaning

3. Agency: U.S. Air Force

4. Laboratory: Wright Laboratory

5. Project ID: #116

6. Problem Statement:

Project Objective: There are two technical objectives to be achieved by this project: (1) To develop and transition to a using customer a cleaning process for large (and small) aircraft components that do not require the use of water or VOCs. (2) To develop a process that will allow components to proceed directly to the next step in the process for surface cleaning without the need for subsequent treatments involving water or organic solvents. This is a 6.2 project transitioning to 7.8 in the out years. This project will transition into the ALCs with potential to be utilized at other service depots. The project is applicable to Thrust 3.A.2, Metal Working Processes - Cleaning and Degreasing, of the Tri-Service Environmental R&D Strategic Plan.

7. Project Description:

Technical Approach and Risks: Research and development is currently being performed by Ohio State University to study the mechanisms and kinetics of solid state (oils, waxes, particulate and metallic oxides) removal processes that have been identified by Boeing. Various processes were being studied including activated particulates or polymers, starch, CO2 and various inorganic particulates including carbonates and phosphates. However, Boeing has selected sodium bicarbonate as the cleaning process based on test data. Studies include an assessment of how clean components really need to be before they proceed to the next step in their particular processing track. Additionally, under this task, McDonnell-Douglas (MDA-E) is looking at CO2 pellet blasting coupled with UV light and activated oxygen technique to clean Al alloy. Laboratory testing (i.e. wet tape adhesion and salt spray), is being accomplished to define and measure surface cleanliness levels needed for various subsequent processing steps in order to maintain/improve the performance of subsequent operations. This effort should be low risk.

8. Expected Payoff:

The project benefit is improved worker safety, reduced environmental liability, reduced cost of storage, tracking, handling and disposal of hazardous waste and uninterrupted production and repair of metal aircraft components. The total cost savings are difficult to quantify since they are based on a specific cleaning method. This effort will be applicable to commercial aircraft component cleaning. In some instances, elimination of ozone depleting chemicals (ODCs) may

be achieved. This project will support the Air Force goal to reduce hazardous waste generation by 50% by the end of 1999 (1992 baseline).

9. Milestones/Accomplishments:

1. Complete media selection and initial cleanliness trials	12/95
2. Complete process parameters optimization and verification of surface cleanliness.	02/96
3. Complete scale up of processes	05/96
4. Complete bonding, plating and performance validation studies of scaled up systems.	09/96

Work continued on the cleanliness requirements and optimizing process subtasks. In conjunction with a Boeing IR&D project, an valuation of non-ozone depleting analytical technique using the IR&D technique as a basis to evaluate panel that were alkaline cleaned, deoxidized, periodically processed ad primed over a period of several weeks. The panels were tested in an effort to compare our task to the Boeing IR&D activity. A fractional factorial design of experiments were run to evaluate blasting with sodium bicarbonate. The series of experiments were conducted in a grit blasting chamber with Armes sodium bicarbonate blast media. The panels were subjected to wet tapes adhesion testing. The large Blue M cleaning chamber is being modified. The UV lamps and controllers were received and installed in the chamber. An excimer light source which produces light in the UV range is being tested and hopefully will provide for faster plasma mixing, which will enhance affordability of UV cleaning technology.

10. Transition Plan:

This R&D program will be conducted in concert with the Air Logistic Centers and will provide engineering data and process information to allow each user to design and implement a systems and processes which will meet their specific requirements.

Potential users will be an integrated part of the R&D team so that their inputs will be incorporated on a continuous basis into the product development cycle.

11. Funding: $(K)

SERDP	FY94	FY95	FY96	FY97	TOTAL
	900	100	578	200	1,778

12. Performers:

The project will be performed under the technical leadership and direction of the Materials Directorate. The Materials Directorate will award one or more research contracts to industry to perform the development and integration. In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans demonstration to be conducted either at an Air Force Materiel Command Air

Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio. This technical effort will build on recent efforts in cooperation with the European Office of Aerospace Research and Development (EOARD) to develop CO2 laser surface modification technology. Related activities include work on Non-chemical Surface Preparation of metals and thin film deposition technology, the AF Civil Engineering Support Activity (AFCESA) spray casting program and thin film (including sol gel) deposition technology developed for the electronic and commercial construction industry.

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14. Keywords:

Cleaning, Coating, Adhesive Bonding, VOCs, Ozone Depleting Substances, Non-Aqueous

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non-Chromate Conversion Coatings & Sealers for Aluminum Alloys

3. **Agency:** U.S. ARMY

4. **Laboratory:** US Army Research Laboratory - Materials Directorate

5. **Project ID:** #673

6. **Problem Statement:**

The development and implementation of (1) a non-chromate conversion coating for aluminum alloys and (2) an alternative sealing treatment to the currently used sodium dichromate in the anodizing process for use in combat and tactical vehicles, munitions, and aircraft.

Toxic chromium emissions are released during anodizing of aluminum. Liquid and solid wastes containing chromium are also generated which contribute to the hazardous waste problem at manufacturing and maintenance facilities. The overall program consists of three major tasks. The first task (Laboratory Evaluation) was previously funded in FY93. This proposal covers the as yet unfunded tasks and demonstrates the use of both non-chrome sealers and non-chromate conversion coatings. The non-chrome sealer will replace the current sodium dichromate sealer which has been one of the most widely utilized sealers for the aluminum anodizing process. It is also anticipated that a non-chrome sealer could be compatible with a non-chromate conversion coating.

7. **Project Description:**

Submitted against 3.A, Metal Working Processes, Subthrust Plating and Finishing 3.A.3, req. # 3.1.c, Heavy Metals Reduction/Elim. from Surface Protection Processes.

Background - Chromate conversion coatings such as the currently specified Alodine treatment have been identified as a large unacceptable source of hazardous waste generation and danger to worker health and safety. Chromate conversion coatings have been utilized to promote adhesion and corrosion resistance of organic coating systems (primer-topcoat). But efforts to develop finishing systems that do not incorporate a pre-treatment have not demonstrated comparable performance.

Another source of unacceptable hexavalent chromium is the sodium dichromate seal used in the aluminum anodizing process. Removal and disposal of the additional hexavalent chrome from the process waste water exacerbates the cost and the potential health safety problem. The use

of a non-chromate sealing system will permit an anodizer to eliminate one hazardous constituent.

Technical Approach - (1)Evaluate by a comprehensive characterization of candidate non-chromate conversion coatings (industrial sources and in-house development) for Aluminum alloys 2519, 5083, and 7039 for comparison with the currently used Alodine chromate conversion coatings. Test protocol includes Auger, ESCA and IR spectroscopy analyses, Salt fog, Electrochemical Impedance Spectroscopy, adhesion, stress corrosion cracking, outdoor exposure and field tests. This project is considered to be of moderate risk.
(2) Several sources of supply for the non-chrome sealer will be identified and evaluated in the laboratory with respect to corrosion resistance, abrasion resistance adhesion, fatigue life. Comparable tests will be conducted in the actual production environment to demonstrate performance equivalent to chromium sealers. Nonchrome sealers for the aluminum anodizing process have been available for many years; however, their performance compared to the chromium based sealer has been inadequate for military and commercial applications requiring maximum corrosion resistance. Recent formulations of some nonchrome sealing chemicals claimed comparable performance to the chrome sealer. The previous FY93 funding covers the laboratory testing to evaluate several potential non-chrome sealers. This proposal covers the technology demonstration and production trial which consists of proving out the non-chrome technology on production equipment at the production rate.

8. Expected Payoff:

Potential users include MSC's, RDECs, Depots, DoD industrial base. The P.I. of the project is a member of the Aerospace Chrome Elimination Group comprised of Army, Navy, Air Force, and industry participants (Boeing, Grumman, McDonnell Douglas, Northrop, Rockwell, Lockheed, Hughes). Use of the non-chromate conversion coating and sealing system will allow government and industry facilities to eliminate one source of hazardous waste with concomitant cost savings associated with reduction of waste treatment and disposal costs. The potential health safety problem associated with hexavalent chromium (a carcinogen) exposure to workers will be mitigated. Though an exact cost benefit analysis is not yet available, the minimal implementation costs foreseen produce a high potential for significant cost savings. In 1991 the Army's cost of safe handling and disposal of hazardous waste was estimated to be $335M. The same cost was projected to be $75B throughout the industrial base.

9. Milestones/Accomplishments:

1. Non-chromate conversion coating (ARL-MD)	Completed(C)
2. Complete industry survey.	02/94C
3. Obtain coated coupons for laboratory evaluation.	06/94C
4. Complete initial Laboratory analysis.	09/94C
5. Downselect conversion coatings for field trials.	09/94C
6. Outdoor exposure tests, field tests.	09/95

7. Specification, transition to users.	09/96
8. Non-chromate sealer (ARDEC)	Completed(C)
9. Complete industry survey.	02/94C
10. Complete feasibility testing.	04/94C
11. Complete laboratory testing.	09/94C
12. Initiate technology demonstration.	02/94C
13. Complete technology demonstration.	10/95C
14. Complete production trial	09/96

One candidate non-chromate conversion coating has shown 312 hours salt spray resistance on alloy 2519. Several non-chrome sealers have shown good performance. From results to date, it is expected that transition of both sealers and conversion coatings will be possible, though certain alloys may be excluded.

10. Transition Plan:

Coordination with MSCs, RDECs, Depots through membership in Corrosion Prevention Advisory Teams (CPATS) and the Aerospace Chrome Elimination (ACE) Group; Coatings sub-panel Project Reliance; introduce specification for non-chromate conversion coating for aluminum alloys early in the acquisition cycle of a weapon system and insure flow-down to contractors, sub-tier suppliers and vendors.

Once a nonchrome sealing system has been successfully demonstrated in the production environment, the technical agency will direct the contracting officer to permit the use of the qualified nonchrome sealing system on aluminum components. Transition to the nonchrome sealing system will require draining and cleaning of the current sealing tank,
to remove any residual chromium, and refilling with the tank with the designated nonchrome solution.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	245	300	68	172	795

12. Performers:

Department of the Army, Army Research Laboratory Materials Directorate, AMSRL-MA-CC U.S. Army, ARDEC, ATTN: SMCAR-CCH-P, Picatinny Arsenal, NJ and Production Installation.

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14. Keywords:

Anodizing, Chromate, Conversion Coatings, Chrome Sealer, Nonchrome Sealer, Sanchem Boehmite, Hexavalent Chrome Reduction.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Aircraft Maintenance Chromium Replacement

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX)

5. **Project ID:** #66

6. **Problem Statement:**

To replace chromates (Cr) currently used in aerospace materials and processes on Navy aircraft (A/C), weapon systems (WS) and support equipment (SE). Chromium VI is a carcinogen. Federal, state and local environmental agencies (EPA, California's Air Quality Management Districts (AQMD), etc.) are restricting the use and disposal of this hazardous material through regulations such as the Clean Air Act, Clean Water Act, and RCRA along with local EPA and AQMD rules. In addition, CNO directives require significant reductions in the amount of hazardous waste generated by the Navy. Chromated materials used in production and depot level maintenance operations are a large contributor to this overall waste generation. Therefore, in order to comply with these regulations while maintaining aircraft performance and operational readiness, chrome-free alternatives have to be developed. This work is covered under the Tri-Service Environmental Quality Strategic Plan, Pillar 3 Pollution Prevention: Requirement Thrust: 3.1.3.e: Non-Hazardous Alternatives for Heavy Metal Constituents Used in Plating and Finishing and is a continuation of an existing SERDP 6.2/6.3 environmental effort.

7. **Project Description:**

Non-chromate alternative materials and processes will be investigated for current anodizing, pretreating, and adhesive bonding processes for aluminum (Al). The approach taken for the development of non-chromate materials will be identification, development, test & evaluation, demonstration and implementation. Chromic acid anodizing (CAA) is a common inorganic coating for pretreating aluminum prior to painting. As an example, this program identified the best alternatives to CAA from existing and developmental coating methods. These alternatives included thin sulfuric, phosphoric, regular sulfuric, and Boeing Aerospace Corp's Sulfuric-Boric Acid Anodize (SBAA). Selected alloys were processed and tested to determine which replacement systems provided equivalent corrosion resistance and paint adhesion while maintaining the existing mechanical properties provided by CAA. After lab optimization, a SBAA production process was demonstrated at the Naval Aviation Depot (NADEP) at North Island. After successful completion of the service demonstration, the Anodize specification was revised (MIL-A-8625F) and SBAA was implemented full scale at NADEP North Island. The LMTCE is currently pursuing full scale transition of SBAA to the fleet. This approach was also

successfully taken for the implementation of non-chromated alkaline cleaners and deoxidizers (previously transitioned materials), and will be taken for the development of non-chromated pretreatments and aerospace adhesive bonding processes and materials.

8. Expected Payoff:

The elimination of chromic acid anodizing, chromated pretreatments and adhesive bonding materials for Al, significantly reduces the total amount of chromium emitted from Navy operations. Elimination of chromic acid anodizing and pretreating materials also eliminates the need for expensive emission control equipment (estimated at $1M per Depot facility) required by CAA and AQMD legislation. Non-chromated alkaline cleaners and deoxidizers, developed under a Pollution Abatement funded program have been implemented at three NADEPs to meet these new regulations. NADEP Jacksonville has reported an annual cost savings of $23K and a reduction of 3 tons of chromium waste per year from the use of the non-chromate deoxidizer. Furthermore, these alternatives significantly reduce rising disposal costs of chromium from Navy operations. This effort is in direct support of Navy and DOD hazardous waste minimization policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, WS and SE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to commercial airlines, automotive industries, equipment manufacturers, etc.

9. Milestones/Accomplishments:

1. Evaluate/optimize Non-Cr acid anodize processes	12/92
2. Initiate non-Cr adhesive pretreatment development	12/92
3. Service demonstration & anodize spec revision (non-Cr)	08/93
4. Evaluate non-Cr adhesive pretreatments	12/93
5. Implementation of non-Cr anodize	03/94
6. Optimize non-Cr Al adhesive pretreatments	09/94
7. Initiate non-Cr adhesive bond primer development	12/94
8. Development of advanced non-Cr conversion coatings	06/95
9. Evaluate non-Cr adhesive bond primers	09/95
10. Initiate service demo of non-Cr Al adhesive bond treat	03/96
11. Service demonstration of non-Cr conversion coatings	08/96
12. Complete non-Cr Al adhesive bond treatment demo	11/96
13. Optimize non-Cr adhesive bond primers	12/96
14. Complete non-Cr conversion coating demo	06/97
15. Transition of non-Cr Al adhesive pretreatments	08/97
16. Service demonstration of non-Cr adhesive bond primers	09/97
17. Transition of non-Cr conversion coatings	06/98
18. Validation of non-Cr adhesive bond primer	08/98

MIL-A-8625 Revised to include both Sulfuric/Boric Acid (IC) and Thin Film Sulfuric Acid (IIB) Types as Alternatives to Chromic Acid Anodizing to meet proposed Clean Air Act Rule.

Technology has been implemented at NADEP North Island, and is in progress at the other Depots. Transition to entire aerospace industry via the spec revision.

A study completed last fiscal year showed that the Boeing Boric Sulfuric Acid Anodize (BSAA) process was not effective as a prebonding treatment. The surface does not have the long term durability of Phosphoric Acid Anodize (PAA); the replacement for Chromic Acid Anodize (CAA). A modified version of BSAA (Rohr SBAA process) was also investigated. The SBAA surface also does not have the long term durability and stability of PAA on 2024-T3 aluminum. Investigation of alternative bond primers has continued this year. Although initial results showed a low temperature peel strength problem with the leading candidate, a reformulated version solved this problem. This work has been coordinated with the Industrial Primers Group (IPG). Phosphoric Acid Anodize (PAA) has shown the best stability of non-chromated pretreatments for aluminum alloys.

Initial studies of EA 9289 primer from Dexter, Hysol showed thickness sensitivity, however, this problem has been resolved. PAA utilized in conjunction with water-borne non-chromated primer EA 9289 has demonstrated the most promising test results versus chromated solvent primer from the initial testing. Large scale testing is scheduled for 1996. BR 6747 low VOC primer had shown the best lab batch scale material properties on PAA surfaces. However, production scale batches of 6747 has shown reduced corrosion resistance within the adhesive bondline. Further testing is scheduled to commence in 1996.

A joint effort with Electrosteam Generators is continuing to optimize a prototype for spray application of the Sanchem non-chromate conversion coating process. Testing on the steam equipment based operation for applying the surface treatment is in progress. In addition, this process has been transitioned to the National Defense Center for Environmental Excellence for production level scale-up for component parts. This demonstration effort is currently in progress.

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at Naval Aviation Depots (NADEP) facilities and transitioned to fleet use through specification modification, technical manual revision and design changes. The Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX) has technical responsibility over the applicable military specifications and technical manuals requiring modification or revision. Industry coordination through out the development and evaluation of these materials will insure availability for implementation. For example, non-chromated alkaline cleaners and deoxidizers have been fully implemented at three NADEPs to meet these new environmental regulations. The SBAA process has been successfully implemented at NADEP North Island and is currently being transitioned to other fleet activities.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	180	158	193	350	881

12. Performers:

Evaluation/demonstration of Chromium-free alternatives is being performed/directed by the Naval Air Warfare Center Aircraft Division Patuxent River (NAWCADPAX) in conjunction with the Naval Air Systems Team. This Team consists of the Naval Air Systems Command, NAWCADPAX, the NADEPs (North Island, Cherry Point, and Jacksonville) and the Lead Maintenance Technology Center for Environment. Headquarters, laboratory and field personnel are all supporting this project. In addition, this effort is being coordinated with the Army Research Laboratory, the Air Force (Tinker ALC, WPAFB Materials Lab and Tyndall AFB Civil Engineering Services Center), National Defense Center for Environmental Excellence (Non-Chromate conversion coating demo) aerospace industries (Boeing, Rohr, Grumman, MDA, etc.) and technical societies (Aerospace Chromium Elimination Team).

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14. Keywords:

Chromium Elimination, Pretreatments, Materials Substitution, Surface Preparation, Anodizing, Adhesive bonding

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non-Chemical Surface Preparation

3. **Agency:** U.S. Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)

5. **Project ID:** #130

6. **Problem Statement:**

State-of-the-art surface treatments for aluminum and titanium alloys generate large amounts of wastewater within the process and/or incident to waste treatment. Treatment processes themselves require the use and handling and hazardous acids and bases, and they often require the use of other undesirable substances such as hexavalent chromium and volatile organic compounds (VOCs). Further, the overall increased emphasis on reduction of VOCs and air toxic emissions will dramatically increase the wastewater stream from surface preparation processes. Management, treatment, and disposal of these hazardous materials and wastes are increasingly costly, burdensome, and constantly attended by the risk of enforcement actions by local, state, and federal authorities.

The development of metal surface preparations that do not require use or generation of hazardous substances and that minimize wastewater streams is needed.

7. **Project Description:**

Technical Objective: The objective is to identify, develop, and optimize new approaches for the formation of stable morphologies on the surface of aluminum and titanium materials that will allow performance of high quality coating or adhesive bonding. Ultimately, the goal is to develop surface preparations for aluminum and titanium alloys that eliminate or minimize use of hazardous materials found in conventional cleaning and surface treatment processes, such as hexavalent chromium, strong oxidizing acids or concentrated bases. Non-wet chemistry approaches or those that greatly minimize the use of water will be pursued in order to reduce or eliminate wastewater streams.

Technical Approach: This program will involve laboratory R&D in several technical areas: plasma spray, sol-gel deposition, ion beam enhanced deposition (IBED), excimer laser treatment, and plasma polymerization. These approaches are based on new technology and initial feasibility has been demonstrated; in many cases, they are currently used for other final applications. These new approaches represent a radical, but environmentally benign, departure from existing surface preparation technology.

The most promising technologies will be optimized, scaled-up, and transitioned to the end-users. There are no serious technological roadblocks foreseen in the scale-up of these processes. Testing will be conducted to verify the various contractor's results and ascertain the level of repeatability with respect to both strength and durability for both adhesive bonding and coating applications. This testing will also allow comparisons between competing processes to be conducted on an equal footing. These tests will form the basis for selecting the most important projects.

The program technical risks include the ability to produce the proper surface chemistries and morphologies with the requisite thermodynamic and chemical stability as well as the needed mechanical strength without degrading the substrate mechanical properties. Attending these risks are the challenges of developing technology that will be environmentally acceptable and affordable. Promising solid state cleaning processes (Project ID #116-USAF) will be tested in conjunction with the best non-chemical surface preparation processes.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.B.1
Requirements Category:	I.4
Work effort:	Tech Base

8. Expected Payoff:

Breakthrough technologies to prepare metal surfaces in various stages of manufacturing and remanufacturing will be of enormous benefit to aerospace and other industries in the US and worldwide. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, they may be offset by eliminating the costs of hazardous materials and waste management and environmental compliance and response. It has been demonstrated that environmentally benign alternative materials and processes can be less costly, more effective, and less time consuming than the technology replaced. Although there is a risk of adverse cost, performance, or schedule impact, the technical effort will endeavor to eliminate or minimize any such impact. This project will support the Air Force goal to reduce hazardous waste generation by 50% by the end of 1999 (1992 baseline).

9. Milestones/Accomplishments:

1. Project go-ahead	08/94
2. Initiate laboratory development and tests of candidate materials and processes Define processes to be replaced and applicable specifications and standards. Define process mechanisms and critical process parameters	10/94
3. Select candidate processes for more extensive testing	12/94
4. Select most promising materials and processes for more extensive testing.	04/95
5. Initiate large laboratory scale process studies. Initiate process parameter sensitivity studies	10/95
6. Initiate studies on surface stability and strength. Initiate coating and bonding studies	10/95

7. Complete all preliminary tests and studies. Initiate scale-up to pilot scale process facility 12/95
8. Initiate extended testing for strength and durability 12/95
9. Initiate optimization of pilot scale processes 03/96
10. Begin treatment of customer furnished components for extended service evaluation 05/96
11. Complete all testing 07/96
12. Prepare documentation, including specifications and standards, as required 09/96

Feasibility has been shown for several technologies to provide surface preparation for aluminum and titanium prior to adhesive bonding or coating. Optimization of the processes to improve long-term environmental durability has met with some success, although further work is needed in this area.

Comparison testing was conducted between the candidate processes and state-of-the-art controls. This testing was helpful in the selection of the most promising candidates for continued optimization and scale-up. Plasma spray, sol-gel and plasma polymerization processes were selected for further development, and work in the area of scale-up has commenced. Sol-gel deposition technologies appear to be particularly well suited for scale-up, and are capable of providing good surface preparations for both adhesive bonding and coating of aluminum as well as titanium.

10. Transition Plan:

The proposed R&D program will be accomplished in an integrated program development mode. The pilot plant will be operated at the Developmental Manufacturing and Modification Facility (DMMF) at Wright-Patterson AFB, OH or at one of the Air Logistics Centers in cooperation with a user team. Successful service experience along with specifications and standards will enable each prospective user to implement processes meeting their specific needs. Potential users will be an integral part of the R&D team to ensure that their inputs will be incorporated on a continuous basis into the technology development cycle.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	300	998	274	641	2,213

12. Performers:

The project will be performed under the technical leadership and direction of the Air Force Material Command, Aeronautical Systems Center, Wright Laboratory, Materials Directorate (WL\ML), Wright-Patterson AFB, OH 45433.

The Materials Directorate will award multiple research contracts to industry to perform the development and integration.

Major performers include Boeing Defense and Space Group, Chemat Technology, Foster-Miller, Lockheed Martin and Cortest Columbus Technologies.

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14. Keywords:

Coating, Bonding, VOCs, Hazardous Air Pollutants, Corrosion Protection, Ozone Depleting Substances

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Recycling/Purification of Plating/Cleaning Baths

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Facilities Engineering Service Center (NFESC)

5. **Project ID:** #70

6. **Problem Statement:**

The goal of this effort is to develop innovative techniques for prolonging process bath life and for recycling hazardous materials from spent process baths to reduce the generation of hazardous wastes (HWs). DoD electroplating shops use process solutions containing hazardous materials for plating, metal stripping, acid etching, alkaline cleaning, anodizing, and other metal finishing operations. The effective life of these solutions is limited by the increasing levels of contaminants that are dragged in from the parts being plated or cleaned. These contaminants reduce plating and cleaning efficiency and will eventually adversely affect the quality of the metal finishing operation. As a result of this contamination, the "spent" bath must be periodically dumped. Large volumes of concentrated HWs are generated from these process solutions that become spent due to buildup of contaminants.

Based on Navy data collected for CY-90, the largest volumes of spent process baths in decreasing order included sodium hydroxide, chromic acid/sodium dichromate, hydrochloric acid, cyanides, sulfuric acid, nitric acid, electroless nickel and nickel sulfamate. While ongoing RDT&E efforts to develop new technologies for eliminating chromium and cadmium (cyanide) plating operations will reduce the use of these particular process baths, many of the alternative processes will still require purification (i.e. replacement of chromic acid anodizing with sulfuric-boric acid anodizing, replacement of cadmium plating with zinc-nickel plating, use of electroless nickel coatings in place of hard chromium plating). Development of alternative application techniques such as spray casting which eliminate the use of chemical process solutions are in the developmental stages and not currently available. Cleaning and stripping solutions will continue to be used. In addition, many new aqueous cleaning solutions are being used to eliminate solvent cleaning with CFCs. These cleaning solutions will require purification to maximize the solution life.

Separation technologies such as ultrafiltration, ion exchange, electrolysis, membrane electrolysis, electrodialysis, and diffusion dialysis will be investigated for use in removing contaminants from plating/metal cleaning process baths. This effort will address a variety of process solutions and removal of different contaminants that buildup. The process baths requiring purification will be prioritized based on DoD volumes of solution waste generated, disposal costs, toxicity, and continued use. The impact of ongoing RDT&E efforts to eliminate chromium and cadmium plating will be considered as well as anticipating requirements for purification of alternative

process baths. Several technologies will be developed for specific applications as required. Test and evaluation of purification technologies with applicability to a variety of process baths will be given the most emphasis. Purification of alternative plating solutions will be considered in the test program.

This project is an ongoing SERDP effort. The Navy effort was enhanced under FY93 funding as a joint Navy/Air Force/EPA project. It addresses SERDP Thrust 3.A.3.a Pollution Prevention for Metal Working/Plating and Finishing. It supports the SERDP goal to minimize or eliminate hazardous wastes through improved in-process treatment technologies for key industrial operations, including metal preparations.

7. Project Description:

The objective of this effort is to develop effective methods and on-line systems for purification/rejuvenation of electroplating (chrome, nickel, electroless nickel, copper, etc), anodizing, and metal cleaning solutions (acids, alkalies). Data will be collected from DoD plating shops to identify the contaminant levels for major process baths and current bath maintenance practices. Contaminant buildup in alternative process baths under test demonstration will also be investigated. Separation technologies such as membrane electrolysis, electrodialysis, ion exchange, and ultrafiltration will be investigated for removal of metal and/or organic contaminants from plating and cleaning solutions. An assessment of technologies completed by the Navy in FY92 will be updated and expanded to identify the status and applicability of emerging technologies for purification/rejuvenation of Navy and Air Force process solutions.

Laboratory tests will be conducted as needed to evaluate alternative technologies. The most promising technologies will be identified for each major process solution disposed by Navy and Air Force plating operations. Field testing of selected technologies will be performed to determine the effectiveness and to optimize design and operational parameters for each purification system developed for specific process baths. Appropriate planning, design, operation, and maintenance criteria will be developed for technology transfer of each system to DoD plating operations and coordinated with American Electroplating and Surface Finishing (AESF) society for transfer to private industry. The technical risk of this effort is low. The project addresses the Tri-Service EQ Strategic Plan, Requirement I.3.b. Reuse/recycling of hazardous wastes generated from electroplating operations.

8. Expected Payoff:

Development and demonstration of bath purification technologies will provide in-process treatment of plating, acid etching, pickling, alkaline electrocleaning, chromating, anodizing, and other solutions. Hazardous wastes generated from these metal finishing processes could be reduced by 75% with the extension of process bath life. Navywide hazardous wastes could be reduced by 375,000 gal/yr providing a savings of $1.3M per year or more depending on the cost for disposal. In addition, cost savings for chemical replacement is estimated at $1.5 M/yr. DoD-wide savings would be at least tripled. The anticipated non-economic benefits include improved product quality of finished parts by reducing contamination in the plating/cleaning processes and

reduced liability associated with hazardous waste transportation and disposal. Users include Navy and DoD plating shops as well as many potential users of this technology in the public and private sectors. As there are many thousand electroplating and surface finishing facilities in the US, there is high interest and potential for transfer to industry.

9. Milestones\Accomplishments:

1. Collect DoD Plating Shop Data	01/94
2. Complete review of advanced and emerging separation and organic destruction technologies.	03/94
3. Identify technology alternatives for each major process bath and prepare updated technology assessment report	09/94
4. Develop experimental design for laboratory and field evaluations to address technology/process bath matrix	06/94
5. Conduct feasibility studies - Alkalinecleaner recycling and electroless nickel rejuvenation	09/95
6. Complete feasibility studies - Chrome purification and acid recovery	03/96
7. Prepare feasibility reports	03/96
8. Optimize design	03/96
9. Conduct field testing - Alkaline cleaner recycle	02/96
10. Select field site for electroless nickel rejuvenation	08/95
11. Contract award to A.D.L. for electroless rejuvenation test	10/95
12. Complete prototype design of electrodialysis system for EN rejuvenation	12/95
13. Electrodialysis installation	12/95
14. Test of electroless nickel rejuvenation complete	03/96
15. Prepare test report and user's guide on electrodialysis	04/96
16. Select site/coordination of acid recovery testing	04/96
17. Contract award for acid recovery	05/96
18. Design and procure acid recovery equipment	07/96
19. Conduct acid recovery field tests	10/96
20. Prepare test report and technology user's guide	12/96

Based on a survey of DoD plating shops, and a technology assessment, the four process solutions types most commonly discarded due to contaminant buildup and the most feasible associated bath purification technologies are: 1) mineral acid etches - resin adsorption, diffusion dialysis, and electrodialysis; 2) alkaline cleaning solutions - crossflow ultrafiltration; 3) electroless nickel (EN) plating baths - electrodialysis, and chemical precipitation; and 4) chromic acid solutions - electrodialysis. Laboratory scale feasibility studies with a crossflow filtration process for removal of oil and grease from alkaline cleaners, and the use of electrodialysis to rejuvenate spent EN plating baths have been completed, and have transitioned to field demonstration projects. Field demonstration of a crossflow filtration system is ongoing at the Naval Aviation Depot North Island in San Diego, CA. System installation, startup, and 140 hours of operation during first test run completed. Three additional test runs are planned. Startup of field projects with an electrodialytic process for EN rejuvenation project utilizing electrodialysis is pending results of a site selection study. Laboratory scale feasibility studies are underway with resin adsorption,

and diffusion dialysis for purification of mineral acid solutions. Field demonstration of a preferred technology will commence pending results of the feasibility studies. Processes based on electrochemical reactions were considered most feasible for purification of chromic acid solutions based on their capability to both remove dissolved metal contaminants and oxidize trivalent chrome back to its desired hexavalent state. Field test projects with four alternative configurations were planned. To date, two have been completed, and the remaining two test efforts are underway.

10. Transition Plan:

Documentation covering planning, design, operation, and maintenance of bath purification systems will be prepared for technology transfer to Navy and DoD activities. This technology transfer package will be published as a final deliverable. The technology transfer package will be provided to appropriate Navy, Army, and Air Force activities for implementation including Air Force's System Program Office and the Technology Transfer Division of Air Force's Center for Environmental Excellence. Private industry will have access to the information developed and, with it will be able to apply the technology as desired. In addition, the capabilities of EPA's Center for Environmental Research (CER) will be used to provide technology transfer of information to private industry.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	600	800	360	440	2,200

12. Performers:

The performers include the Naval Facilities Engineering Service Center with joint participation from Air Force's Wright Laboratory, Manufacturing Technology Division and EPA's National Risk Management Laboratory. Wright Laboratory will assist in the collection of plating shop data, development of contracted efforts for pilot and field testing, and identification and coordination of field tests at selected Air Logistic Centers. NRML will assist in laboratory and bench scale studies of advanced membrane technologies that could be applied to process bath purification and in transfer of technology to private industry. The POCs for partners in this effort are Mr. Roger Wilmoth, NRML, Toxics Control Branch, (513)569-7509 and Mr. Dan Brewer, WL/MTX, (513)255-36701 x208.

13. Principal Investigator:

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14. Keywords:

Electroplating, Metals Removal, Membrane Separations, Purification

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** PVD and Ion Beam Processes To Replace Electroplating

3. **Agency:** U.S. ARMY

4. **Laboratory:** U.S. Army Research Laboratory - Materials Directorate

5. **Project ID:** #632

6. **Problem Statement:**

Eliminate or reduce usage of environmentally harmful chrome and cadmium electroplating processes. Conduct applied research and development to demonstrate that metal or ceramic coatings deposited by physical vapor deposition (PVD), and/or ion-beam-modified surfaces are equivalent or superior in performance and are a cost-effective & environmentally acceptable alternative to electroplated Cr and Cd for military applications.

7. **Project Description:**

Submitted against 3.A, Metal Working Processes, Subthrust Plating and Finishing 3.A.3, req. # 3.1.c, Heavy Metals Reduction/Elim. from Surface Protection Processes.

Background - Hard chrome is primarily used in DoD related manufacturing to (1) coat high wear surfaces such as bearing shafts and hydraulic components and is principally performed by Original Equipment Manufacturers (OEM's) and (2) rebuild and remanufacture of out-of-tolerance components at maintenance depots. For the former, the use of hard chrome has actually been increasing because of the general requirement enhanced performance. For the latter application, many components are returned to the depots for refurbishment that are worn, corroded, or eroded by use. The components are reworked by removing the damaged metal, stripping off any old hard-chromium coatings, building them up with hard-chrome, and then machining them to final tolerance. Corpus Christi Army Depot (CCAD) coats more than 10,000 types of components annually with hard-chrome for this purpose. Most of these components are re-plated several times during their service lives.

Gun tube wear & erosion have been a long-standing military unique problem. A practical objective has been to achieve gun tube wear life comparable to fatigue life, though wear & erosion caused the unexpectedly short tube life for the new 8" and 155 mm gun systems. Advanced gun systems under development (such as Liquid Propellant and Rail Guns) will push requirements to even higher standards. New protective coatings with even higher melting points (refractory metals) are needed to challenge the use of more energetic propellants with higher flame temperatures.

Cadmium electroplating is also used by both OEM's and by DoD maintenance depots to impart corrosion resistance and lubricity to a wide variety of parts, although several alternatives exist for certain applications. These alternatives include electrodeposited Zn and Zn alloys and ion-vapor-deposited (IVD) aluminum. The Anniston Army Depot, Anniston, AL, has recently installed two IVD systems and is replacing Cd with IVD-Al for some components of armored vehicles. CCAD has also recently installed an IVD system, and is currently replacing Cd on many non-flight critical parts. An Air Force study acknowledges that IVD-Al will not easily replace more than about 50% of the Cd-plating requirements. The Army has authorized electroplated zinc as an alternative to cadmium for grade 8 fastener application. Exceptions include selected electrical/electronic applications where Cd-plated fasteners are required and high strength steel components. A recent study by the Army Research Laboratory, Watertown Site, showed a Zn-Ni alloy provided better resistance than zinc and exhibited a comparable coefficient of friction. While the Cd plating alternatives have reached a certain degree of maturity, several issues still need to be resolved. The Aviation Troop Command, (ATCOM), St. Louis, recently outlined the problems to be addressed which include: fatigue and Environmentally Assisted Cracking (EAC), torque-tension requirements for fasteners (before and after exposure), close tolerances, and ability to reach recessed areas. Thus there still exists the strong (& urgent) need for further coating development & characterization efforts.

Technical Approach - Vacuum-based PVD coating techniques are known to produce the highest quality coatings, with widespread use of high vacuum techniques in the microelectronics industry having broadened the industrial base for large scale systems with a concomitant reduction in cost. The most advanced types of PVD coating techniques utilize what can be called "ion-assist" whereby energetic charged particles are incident on the workpiece during the coating process. Two variations on ion-assisted PVD are (1) ion-beam-assisted deposition (IBAD) whereby a directed beam of energetic particles from an ion gun are coincident on the workpiece with the depositing vapor atoms, and (2) magnetron sputtering whereby vapor atoms are produced by sputtering from an electrode with ions being accelerated from a plasma by application of a negative bias to the workpiece. These two techniques produce coatings that are highly adherent, fine grained, generally pin-hole free and fully dense, and which can be deposited at relatively low temperatures on virtually any type of solid material. The deposition rates for these types of coating techniques are sufficiently high that they could be expected to economically replace both chrome platings deposited by OEM's and electroplated cadmium. For these applications, the types of coatings to be investigated would be TiN, (Ti, Al)N, CrN, Ta and diamond-like carbon, all of which have been previously investigated for corrosion and wear applications. However, the deposition rates are not high enough to replace the chrome plating operations in military depots which are intended for re-build of components. For this application, the proposed solution is to rebuild the component using an alternative electroplating technique such as electroless nickel, machine it to final tolerance, and then apply one of the above PVD coatings to provide significant wear and corrosion resistance.

Ion implantation has been shown to significantly improve the corrosion and wear behavior of a variety of materials. Virtually any element can be implanted into substrate materials although only a few will be selected for this program. Previous research conducted at ARL has shown that nitrogen implantation into hard-chrome coatings increases the surface hardness and

significantly reduces the tendency of the coatings to form microcracks when subjected to loads or stresses. This will be further investigated under this program as well as ion implantation of thin-dense-chrome coatings, a proprietary of Armoloy, Inc., which is an electroplating process that does not produce toxic effluents. Previous efforts in this area have investigated alternative electroplated coatings, such as Zn alloys as Cd replacements. The only significant exception to this is the development of IVD aluminum. It is interesting to note that large-scale IVD-Al systems have been available for over 16 years, yet DoD is still funding R&D work to investigate and implement this process. Electroless nickel coatings are also being investigated as a replacement for chrome, but nickel is on the EPA "toxic enemies" list so it should be considered as an interim process. An important issue in developing new types of coatings in any system is whether it will have any effect on any other system components. If a chromium coating is replaced with another coating which demonstrates superior performance in laboratory tests, will it have a detrimental effect on its mating part? This potential problem will be considered in the selection and evaluation of actual components. This overall program is considered to be of medium technical risk.

Relationship to Other Similar Ongoing Work - The Basic Industry Research Laboratory (BIRL) at Northwestern University has been awarded a substantial contract ($1.5M over two years) entitled, " Hard-Chrome Coatings: Advanced Technology for Waste Elimination." This proposed SERDP program is designed to investigate other coating techniques and thus there will be virtually no duplication of effort. One of the POC's (BDS) on this proposal has collaborated with the PI on the DARPA contract. Extensive collaboration/coordination between the two programs will ensure that DOD will obtain the optimum solution(s) to this problem. This program is also closely coordinated with the NDCEE demonstration program for Ion Beam Processing. There is currently a proposed ESTCP effort to take both the BIRL and SERDP program results beyond their current 6.2 phase and fully transition the process to the depot level.

Tasks/Activities - The focus of the project will be the characterization and evaluation of the coatings in comparison to electroplated chromium and cadmium coatings. Evaluation of coating performance must include laboratory simulation of battlefield and global environments, with a baseline comparison with hard-chrome coated components. Properties such as hardness, adhesion, and density will be determined for each coating. Measurements related to actual performance will be correlated with the type of electroplated coating intended to be replaced and the actual end-use application. Thus, testing will include 1) sliding wear tests with realistic loads, speeds, and use of lubricants, 2) erosion tests, 3) corrosion tests using electrochemical and/or salt spray methods, and 4) low-cycle or high-cycle fatigue, or rolling-contact fatigue, and 5) hot-hardness tests. In addition to evaluation of coated test coupons, actual components will be selected for coating and evaluation. The POC's have assembled a team to address all of the tasks related to coating deposition, characterization, and evaluation. The tasks are listed with the activities expected to perform them. An (A) or (N) following the activity denotes whether the Army or the Navy will be the primary contact.

Corrosion Science Group, ARL(A): Deposition of IBAD and plasma sprayed coatings; cohesion, adhesion, and porosity measurements on all coatings; surface analytical measurements; corrosion

by electrochemical impedance spectroscopy, galvanic corrosion studies; erosion tests; coefficient of friction measurements; rolling contact fatigue measurements.

Surface Modification Branch, NRL(N): Deposition of IBAD coatings; hardness, density, and adhesion measurements on all coatings; composition measurements on compound coatings and determination of impurities, if any; other surface analytical measurements; sliding wear tests; corrosion tests.

BIRL, Northwestern University: Deposition of magnetron sputtered coatings; high temperature wear tests using Falex tester; deposition of HVOF coatings (A).

-- Jet Process Corporation, New Haven, CT: Deposition of PVD coatings (N).
-- Armoloy of Connecticut, Inc.: Deposition of TDC coatings (A)
-- Naval Air Warfare Center, Trenton, NJ: Fatigue testing of coated samples (N).
-- Corpus Christi Army Depot (CCAD): Deposition of cadmium and chromium coatings onto test specimens; selection of two helicopter components (in consultation with ARL) for coating; rig testing of coated components (A). Flight-test arrangements will be made with the ATCOM and the NASC.

8. Expected Payoff:

Coatings developed under this project should demonstrate performance that exceeds that of electroplated coatings, thus reducing the frequency of rework. This will further reduce the costs associated with the new processes. As an example, if a 2.5 X increase in service life by using ion implantation can be achieved, estimates base on CCAD data show these re-work savings on only three bearings and gears used in the AH-1/UH-1 helicopter drive trains would total over $1.2 M yearly. The potential on a DoD wide basis would be many times greater. It is also intended to use this technology for gun tubes which are routinely Cr electroplated to provide wear resistance the bore. The costs of alternative coating technologies should not be compared with the current cost of Cr and Cd coating, but with their expected future costs, taking into account regulations projected into the future. The Basic Industry Research Lab cost analysis has concluded that for operations with equivalent throughput, the operating cost for a PVD facility would be 20% less than for a plating operation (based on info. from CCAD, McClellan AFB and on their own calculations for PVD operations).

9. Milestones/Accomplishments
(C denotes completed objectives as of 11/95)

1. Test coupon fabrication	07/94C
2. Coating applic. to coupons	09/94C
3. Lab. wear evaluation	06/95C
4. Lab. electrochem. eval.	06/95C
5. Fatigue evaluation	09/95
6. Salt-Spray evaluation	09/95C

7. Component selection	08/94C
8. Coating optimization ident.	08/95C
9 Coating components	06/96
10. Rig testing	09/96
11. Develop transition plan	09/96
12. Flight testing	09/96

To date, several of the coatings applied have shown wear, adhesion, and corrosion properties equivalent or exceeding that of hard chrome plate. Selection of components for coating in 1996 has proceeded on schedule, and interaction with the BIRL DARPA study has been invaluable.

10. Transition Plan:

A detailed transition plan will be developed early in 1995, in close cooperation with the field activities, CCAD and CPNAD, as well as other activities (Army MSC's and RDEC's, NAWC's, the Joint Technology Exchange Group and the Aerospace Chrome Elimination Group). Additional selected components will be coated, with some subjected to additional rig testing, and the remainder installed in actual operating aircraft. Cherry Point NAD expects to install a large PVD coating system in early 1995, which will coincide well with the technology transition. Since it will not be possible to individually evaluate (qualify) the replacement coatings for every component that is currently electroplated, a key aspect of the transition plan is to provide information and data, including coating deposition specifications, to agency engineers so that new coating technologies can be certified for use in broad areas.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	485	550	218	267	1,520

12. Performers:

Corrosion Science Group, ARL; Surface Modification Branch, NRL; Jet Process Corporation, New Haven, CT; Armoloy of Connecticut, Inc.; BIRL, Northwestern University, Evanston IL; Naval Air Warfare Center, Trenton, NJ; Corpus Christi Army Depot (CCAD), Corpus Christi, TX; Aviation Troop Command, St. Louis & Corpus Christi, TX; Naval Air Systems Command

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14. Keywords:

Hard Chrome, Physical Vapor Deposition, Metal Coatings, Ceramic Coatings, Electroplated Chromium, Ion-Beam-Modified Surfaces, Zinc Alloys, Tin Alloys

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion

3. **Agency:** U.S. Army

4. **Laboratory:** Army Research Laboratory, Aberdeen Proving Ground, MD (ARL)

5. **Project ID:** #680

6. **Problem Statement:**

Goal: To reduce production of waste and unnecessary energetics material in manufacturing for guns and rockets. To completely eliminate inventories of high explosives (RDX, HMX, PETN, TNT), pyrotechnics (blackpowder, lead styphnate, azides) and nitrocellulose-based igniter materials from the inventory of energetic materials used in propulsion through the use of laser radiation as the primary ignition source. To avoid pollution problems associated with the demilitarization/incineration of these materials. One laser can replace thousands of lbs of this material in the life cycle of a gun system.

Background: The chemical ignition materials used in gun propulsion consist of various high explosive, blackpowder, nitrocellulose-based propellants, benite, BKN03 and other pyrotechnics. Demilitarization of the vast inventories of these sensitive materials via incineration is dangerous and can produce pollutants, carcinogens and toxic agents. There are also safety considerations in the manufacture, handling, storage, disposal or recycling of these energetic materials which greatly impact cost. This proposal addresses a means to negate all of these concerns through the development of technology by which propellant ignition materials will be eliminated from DoD inventories. Rather then initiating research to understand or minimize the hazards associated with incineration, advanced laser technology will be utilized as a replacement for large caliber gun propulsion. Problems associated with the disposal of ignition materials will no longer exist when lasers are integrated as the primary gun ignition source.

7. **Project Description:**

The objective is to eliminate hazardous components in ordnance and ordnance manufacturing, to reduce the production of waste and unnecessary energetic materials in manufacturing for propulsion systems (large, medium and small caliber guns, rockets, missiles), to eliminate inventories of primers (containing sensitive energetic materials, lead styphnate, pyrotechnics) and to eliminate hazardous in manufacturing, storage and disposal of these components. The long term goal is to develop a universal ignition system using the laser. The chemical ignition materials used in ordnance/gun propulsion consist of various hazardous materials such as lead styphnate, lead azide, high explosives, blackpowder, nitrocellulose-based propellants, benite,

BKNO3 and other pyrotechnics. The objective of this project is to eliminate these materials from ordnance, eliminate the need for their manufacture, and also avoid pollution problems associated with their demilitarization/incineration (which can be dangerous and produce pollutants, carcinogens and toxic agents). There are also safety considerations in the manufacture, handling, storage, disposal or recycling of these energetic materials which greatly impact cost. In order to reduce hazardous components in ordnance and ordnance manufacturing a laser ignition system will be developed to ignite the propelling charge. The laser is a non-polluting ignition source can replace thousands of lbs of hazardous material in the life cycle of a single gun system.

30 mm Laser Ignition Task:

The 30 mm rapid fire armament is currently fielded on over 800 helicopters utilized by the Army. Medium caliber weapons of this type are used on several other systems in all the services. The current ignition is via an electrically fired primer containing lead styphnate which transfers to 3 IB52 BKNO3/fluid ball pellets(pyrotechnics) which in turn ignite the WC855 double base ball powder. If we can eliminate the primer, IB52 pellets, and flash tube that contains them (for example) a major cost savings would be obtained. There is also the possibility to get good action times at all temperatures (-54C to +71C required). From the perspective of the user, the driver for conversion is to reduce electromagnetic sensitivity. The current ignition system can easily be accidently fired, discharging the weapon. Helicopters that utilize this armament, for example, can create a very dangerous and lethal situation when they land on Navy ships where fields approach 200 volts/square meter. A percussion primer which would accomplish this goal has been designed with a per-gun cost of $4K to $5K. We either need to beat that cost or make the ammo cheaper to fire so that money is saved on that end. More than 700,000 rounds are fired per year (M788TP) on weapons used on just this one armament on helicopters alone. Collectively, tens of millions of rounds are fired by all services. Additional benefits include higher rates-of-fire and full digital control of the laser firing and therefore the weapon.The SERDP objective is to eliminate hazardous components in ordnance and ordnance manufacturing by replacing the current ignition system with the laser.

Demonstrate the feasibility of converting the existing M230 cannon to laser ignition, without degrading the firing rate or compromising any safety features (no fire until round chambered). Modification must be cost effective when compared with other (EMI and RFI safe) alternatives. Specific goals are to demonstrate cartridge modification features by firing the cartridge in a Mann barrel and to show fully automatic operation feasibility by firing a 3 round group in 5 seconds. Eliminate Lead from the ordnance.

8. Expected Payoff:

Potential Users: DOE, DoD, ARDEC, MICOM, Benet, AFAS, Navy, NASA, Air Force, Industry will use technology to eliminate these dangerous and unnecessary materials from their inventories. Dual Use Technology developed such as laser systems, optical components, optical feedthroughs will benefit both military and civilian markets. Four ongoing SBIR programs to develop technology are in place.

Impact: Removal of these materials from current inventories, eliminate environmental pollution, waste and hazard from disposal, immense cost savings from safety considerations in all aspects of manufacture, production waste in manufacturing, storage and handling, benefit to the soldier in the field from a safer and simpler weapons system (less vulnerable).

9. Milestones/Accomplishments:

Large Caliber:

1. Laser parametric investigations (wavelength study (using ruby and alexandrite) to minimize ignition delay.	06/95
2. Design optics package for breech spindle, test direct ignition in small scale ballistics simulator,begin large scale ballistic simulator testing with laser ignited charge.	07/95
3. Development of Mil-Std optical fiber connector, sapphire window materials study, testing.	08/95
4. SBIR: Optical fiber manufacturing, feedthrough fabrication, three compact laser developmental efforts (diode, Nd:YAG, diode-pumped YAG) PHASE I SBIRS COMPLETED	12/95

30 mm Project:

5. Develop concepts for the laser hardware, and the integration of the laser hardware (fiber optic cable assembly, focusing elements, laser unit, control interfaces, etc) on the M230 system. Concepts will be based on outcome of ARL experiments and AED cartridge modification concepts.	11/95
6. In coordination with ARL and AED, rank alternative concepts. Select Best Technical Approach.	12/95
7. Mann barrel tests Single shot.	03/96
8. 3 round group test; full-auto- with laser ignition.	05/96

ACCOMPLISHMENTS:

Large Caliber 155 mm Laser Ignition Task:

Two complete laser ignition systems were developed and tested. One was a fiber coupled system and the other was a breech mounted system.

A massive sapphire window redesign effort was initiated which included a study of the materials properties of sapphire. Recent investigations have revealed a possible failure mechanism that produces (known as Rhomohedral Micro Twinning (RMT) with sapphire orientated along the "C" axis under compressive loading. (Our sapphire windows are oriented with the "C" axis perpendicular to the window face). These results suggest that this orientation is probably the worst choice for sapphire placed under high compressive loads and simultaneously exposed to high temperature. The "C" axis orientation is typically chosen for optical sapphire windows because along this axis the birefringence is minimal. Birefringence causes a light beam (laser beam) to split into components thereby producing a double image. In the case of sapphire with "C" axis orientation, the double images almost fall on top of each other, so this is not a problem for our purpose (ignition). Our gun firings place the sapphire windows under compressive loading; near 50,000 psi with top zone charges. The strength of "C" axis orientation sapphire at room temperature under compressive loading is 300,000 psi. The strength of "C" axis orientation sapphire at elevated temperature (800 C) under compressive loading dramatically drops to around 5000 psi. The combination of high compressive loading (50,000 psi) in our gun firings and high temperature (3000 C) is just the right recipe to produce RMT - our windows crack.

The strength of "A" axis orientation sapphire at room temperature under compressive loading is also around 300,000 psi. However, the strength of "A" axis orientation sapphire at elevated temperature (800 C) under compressive loading does not drop dramatically - its about 270,000 psi. Therefore, if we build windows with "A" axis orientation we might see no cracking or perhaps at worst a lifetime that greatly exceeds 300 EFCs.

This analysis was performed with sapphire windows that were brought up to a temperature of 800 C. The entire sapphire was at that temperature-uniform throughout the bulk material: in thermal equilibrium.

Our sapphire windows with "C" axis orientation are exposed to 3000C, but only for about 100 milliseconds. The entire window bulk material does not equilibrate to 3000C. However, the surface is exposed to this high temperature, albeit for a very short time. Therefore surface RMT is expected. This is precisely what we have seen occurring with our windows. Surface cracks. It has been proposed that we fabricate some windows with an alternate axis orientation ("A") and subject them to high-zone gun firings. It might be a good idea to fabricate windows of an identical geometry with ("C") axis orientation and mount them the same fashion and subject them to high-zone gun firings for comparison.

Near finalized versions of the laser ignition have been determined. A Laser Ignition System (LIS) is under development AS THE MAIN IGNITER for the 155 mm Advanced Solid Propellant Armament (ASPA) System howitzer which will use the Modular Artillery Charge System (MACS). Two LIS versions are under development and are referred to as the Fiber-Coupled LIS (FC-LIS) and Breech-Mounted LIS (BM- LIS).

The FC-LIS consists of a Nd:YAG laser, optical fiber/collimator and sapphire window. The Nd:YAG laser delivers a 12 Joule laser pulse (5 milliseconds in duration) through a optical fiber.

The collimator at the terminal end of the fiber focuses the laser beam into the gun chamber through a sapphire window. The flexible steel-clad fiber cable and collimator will be a single unit that snaps onto the laser and cannon breech block. The sapphire window is sealed in a steel housing which screws into the forward face of the breech block wedge. The objective laser unit should be about 12 x 12 x 9 and about weigh 30 pounds.

The BM-LIS consists of a Nd:YAG laser and sapphire window. The Nd:YAG laser delivers a 12 Joules laser pulse (5 milliseconds in duration) through a sapphire window into the gun chamber. The laser module is mounted onto the breech block of the cannon. Therefore, the optical fiber/collimator unit is not required. An electrical cable or electrical feed through powers the laser module. The sapphire window is sealed in a steel housing which screws into the forward face of the breech block wedge. The objective laser unit should be about 6 x 2 x 2 and weigh about 5 pounds. The objective power supply unit should be about 12 x 12 x 6 and weigh about 20 pounds.

The laser units use either the closed-loop, maintenance-free liquid cooling system currently in use or solid-state cooling units that are under development. The laser rod must be cooled at rate of fire of over 5 rounds per minute. For the BM-LIS, a cooling line, along with the electrical cable, will have to be run from the power supply unit to permit laser rod cooling . In a FC-LIS, 0.5 liters of cooling fluid is currently in the laser unit. In a BM- LIS, an estimated 1 liters of cooling fluid will be in the laser unit, the cooling line and the pump at the power supply unit.

A simple mist, gas jet cleaning system cleans the sapphire window surface after each firing. This system is currently in successful use during cannon testing at YPG. It uses under 0.5 milliliters of cleaning fluid for each shot or under 0.2 liters of fluid for a battlefield day of 349 rounds.

The FC-LIS and BM-LIS can be fully operated by an automatic fire control system. A FC-LIS was demonstrated at Fort Sill in February 1995. All testing to date has been accomplished with the FC-LIS. A proof-of-principle demonstration of the BM-LIS was successfully completed in September 1995. Development of the BM-LIS will accomplished through SBIR contractors in parallel with the evolution of the FC-LIS.

The FC-LIS and BM-LIS offer the following advantages:

1. Elimination of conventional lead containing M82 primer and firing mechanism from the ignition train.
2. Readily support an automatic loading cannon to provide high rates of fire at a cost savings over the M82 primer.
3. Full computer control of the firing mission since the cannon can not be fired unless properly laid in position.
4. Backwards loaded conventional charge will not ignite.

30 mm Laser Ignition Task:

The Army Research Laboratory (ARL) and Army Armament Research, Development and Engineering Center (ARDEC) have initiated a program to demonstrate the modification of the 30mm M230 weapon and ammunition to use a laser as the ignition means instead of direct electric or mechanical power with lead containing igniters. The ammunition currently used in the M230 is the M789 High Explosive Dual Purpose (HEDP) cartridge and the companion M788 Target Practice (TP) cartridge. Both rounds are fired electrically using the PA520 electric primer. The PA 520 primer is, however, susceptible to initiation when placed in an RF field with a strength of 5 volts per meter or higher.

The requirements for the next generation Apache, the D model (also called the Longbow) are for the helicopter to be capable of being loaded and functional in RF field strengths of up to 200 volts per meter. To accomplish this, the 30mm M230 and associated ammunition must be modified. The ARL/ARDEC team are working to modify the required hardware and conduct a single shot demonstration of the ammunition fired with a laser ignition and then conduct a small low firing rate demonstration from a modified M230 automatic cannon. The first of the two demonstrations will be in the first quarter FY96 and will show that the ammunition can be initiated with a reasonably powered laser and still function in a short enough time to meet the time constraints of the current M230 firing rate (625 rounds per minute). The second demonstration will take place in the second quarter FY96 and will be fired with a modified M230 weapon. The firing rate will be reduced to 100 to 200 shots per minute and the burst will consist of three modified rounds. To keep the maximum amount of commonality with the current weapon and thus minimize the modification cost and risk, the laser ignition system envisioned will modify only three operating parts from the current M230, a modified electrical contact box to hold a fiber optic cable, a firing cable holder instead of a firing pin assembly and a modified breech bolt. In addition, the system will have the addition of the firing laser and a fiber optics cable to transmit the laser firing pulse to the cartridge. For the demonstration, the cartridge will be identical to the current M788 TP cartridge except that the lead containing primer will be removed and an initiator window will be installed. The window will allow the transmission of the laser pulse directly to the ignition material from the weapon. The two major benefits of this concept are the elimination of the RF sensitivity and also the elimination of lead from the emissions of the cartridge. The second is accomplished with the removal of the primer, which contains lead styphnate. All other compounds in the round are without lead, thus the round becomes lead-free. Ultimately, it is also anticipated that a cost reduction in the manufacturing of the round could be accomplished with the elimination of the handling and loading of the primer.

Paper Submitted: Title of Paper "30mm Laser Ignition Demonstration" To be Presented, Guns/Ammunition--Revolutionary/Evolutionary Technologies and Systems, 1996 Guns and Ammunition Technical Symposium, March 26-28, 1996, Orlando, Florida.

10. Transition Plan:

Technology will be transferred to ARDEC and coordinated with Benet Labs through 6.3 program.

Relationship to DoD/DOE: To reduce production of waste and unnecessary energetic materials in manufacturing. This proposal seeks to eliminate pollution hazards from propellant materials demilitarization, incineration and recycling by eliminating their need in current applications.

Relationship to Ongoing Work: Participants: ARDEC, MICOM, Benet, PM-AFAS, Navy, China Lake, NASA, Air Force. The defense industry, international defense institutions (Germany, UK) and the US DoD community are utilizing lasers as a means of augmenting propulsion. This represents the first effort to design a propulsion system with the central purpose being the elimination of stockpiles of energetic materials to avoid pollution from demilitarization and incineration. Our preliminary work has demonstrated that the laser can achieve these goals.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	200	313	138	180	831

12. Performers:

This work will be performed at ARL. Demonstration testing will be done at ARDEC.

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14. Keywords:

Laser, Ignition, Propulsion, Primer, Gun, Optical Fibers

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Extraction and Recovery of LOVA Propellants Using Supercritical Fluids

3. **Agency:** U.S. Army

4. **Laboratory:** U.S. Army Research Laboratory

5. **Project ID:** #660

6. **Problem Statement:**

Objective: Solid gun propellants and explosives are currently destroyed by open burning or open detonation (OB/OD). Supercritical fluid recycling would have both economic and environmental advantages over destructive OB/OD processing. Unfortunately, the nitramine ingredients (RDX, HMX) found in many of military explosives and composite LOW Vulnerability Ammunition (LOVA) propellants have insufficient solubility in non-reactive supercritical fluids (e.g., CO_2). The objective of this program is to identify suitable supercritical solvents and processing conditions for the recovery and recycling of the valuable RDX and HMX ingredients used in these munitions.

Background: There are two primary branches in SF technology related to ordnance demilitarization: HAZMAT destruction via supercritical oxidation (SCWO), and carbon dioxide-based supercritical fluid extraction (SFE) for purposes of material reutilization (pollution prevention). The use of SCWO has been under study by various researchers, for a variety of applications, over the last decade (see C&E News, Dec. 23, 1991): the DoD has established a pilot plant that uses supercritical water to destroy military toxic wastes. The conventional ammo demil stockpile currently contains 16M pounds of recoverable nitramine-based explosives, with an amount of RDX exceeding 11M pounds (Source: Demil Task Team Study Report for Congress, Aug. 95). This quantity of RDX has a market value of $50M - $100M, and should be considered a potential resource. For the long term, recovery and reutilization of RDX should be the preferred approach.

7. **Project Description:**

This research originally involved investigations of the effectiveness of polar "modifiers" in increasing the solubility of RDX in supercritical carbon dioxide. The goal was to identify those compounds which "modifiers" that a) significantly increase the solubility of the RDX in supercritical carbon dioxide, b) do not result in hydrolysis or other chemical degradation of the RDX, and c) can themselves be recycled (supercritical fluid extractors can operate closed-cycle), or are as close as possible to neat carbon dioxide in having negligible environmental impact. In

addition to carbon dioxide, several additional polar neat supercritical solvents were investigated for the direct extraction of RDX from LOVA propellant. During FY93 and FY94, polar modifiers were identified which would enhance the solubility of RDX in carbon dioxide by close to two orders of magnitude in the range of 3 mole percent doping.

More recently, emphasis has been placed on the recovery of RDX from explosive munitions such as Comp B (RDX/TNT/Wax). Recent work in our lab has demonstrated that TNT powder can be extracted from RDX powder under relatively mild extraction conditions. Wax should also be much more soluble in supercritical carbon dioxide than is RDX. In this case, it makes more sense to extract these ingredients than the RDX. In this case, we are looking at a process which only involves carbon dioxide as a processing solvent, with no use of organic modifier, although we have not ruled out the use of water as a modifier at a doping (determined by its solubility in carbon dioxide) of around 1 mole percent. By limiting this process to only carbon dioxide and water, this becomes a very environmentally-friendly means for separation of the RDX from the formulated explosive.

The emphasis of our efforts for FY96 is entirely towards explosive formulations, and away from propellants. A lab-scale closed-loop supercritical carbon dioxide extractor has been set up to demonstrate process feasibility on a research series of formulations, including Comp A and Comp B explosives. Since FY96 is the final year for SERDP funding of this project, we will pursue funding through the appropriate government agencies for scale-up and implementation of this work for FY97 and beyond.

8. Expected Payoff:

Prevention of pollution associated with the disposal of Army (and Navy) propellants and explosives; associated reduction of life-cycle cost of munitions. Over half of the of the recoverable nitramine-based explosive in the conventional ammo demil stockpile is Comp B, with a RDX market value of \$25M - \$50M.

9. Milestones/Accomplishments

FY96 Milestones:

1. Demonstrate lab-scale RDX separation process for Comp B	09/96
2. Receive hazards assessment report	09/96
3. Release project summary report	03/97

Major Project Accomplishments (FY93-FY95):
During the early years of this project, we were interested in the direct extraction of RDX using polar modifiers for carbon dioxide. The relative effectiveness of over 30 modifiers for direct extraction of RDX has been determined, along with some factors which can be used for predictive screening of other modifiers. With our more recent emphasis on the separation of RDX from explosives, we have measured the solubility of RDX in neat supercritical carbon dioxide in the expected processing ranges of temperature and pressure. In addition, we have

demonstrated the feasibility of selective removal of TNT from a TNT/RDX powdered mixture, with a TNT:RDX selectivity of about 30:1.

10. Transition Plan:

Progression is from 6.1 research into solubility relationships and modifiers (through FY94), then 6.2 research into extraction/recycling schemes beginning in FY95. Future plans for technology transfer include a pilot plant demonstration, possibly at the Naval Surface Warfare Center (NSWC), Indian Head, MD, where large-scale supercritical fluid processing facilities are scheduled to be on-line sometime during FY97.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	400	450	248	300	1,398

12. Performers:

Most research (6.1, 6.2) is being carried out in-house at ARL.

During FY93 - FY95 there were small contracts for technical support and instrument development with the AppliTech Corporation (Nottingham, PA: FY93, FY94, FY95), CCS Instrument Systems, Inc. (Avondale, PA: FY93, FY94), the CECON Group (Wilmington, DE: FY94, FY95) and the Johns Hopkins University/Chemical Propulsion Information Agency (CPIA, Baltimore, MD: FY95). Contracts with CPIA and the AppliTech Corporation will also be utilized during FY96. Sponsorship for scaleup in FY97 and beyond will be sought from the Demilitarization Technology office at the U.S. Armament Research, Development & Engineering Center (ARDEC). Pilot-plant demonstration (FY97) will be carried out using NSWC facilities, or facilities at a site determined by ARDEC. Related Activities: This project is being closely coordinated with related projects at MRDEC (MICOM) and NSWC. In addition, we maintain unfunded technical interaction with ARO contractors, as well as other national laboratories involved with supercritical fluid technology, such as Los Alamos National Laboratory.

13. Principal Investigator:

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14. Keywords:

Explosives, RDX, TNT, Demil, Recycling, Supercritical Fluid Extraction

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Recycling Propellants in Nonpolluting Supercritical Fluids; Novel Computational Chemistry Models For Predicting Effective Solvents.

3. **Agency:** U.S. Army.

4. **Laboratory:** U.S. Army Research Laboratory - APG.

5. **Project ID:** #695

6. **Problem Statement:**

Waste solid explosives and propellants are destroyed primarily by open pit burning or incineration. Extraction and subsequent recycling of the explosive and propellant components, as opposed to destruction, using a non-polluting, inert supercritical fluid (SCF) solvent would have obvious economic and environmental advantages. The components of composite solid LOVA propellants [an energetic material such as RDX, HMX or TNT, and polymeric binder] have very low solubilities in an inert SCF solvent such as carbon dioxide (CO2), making the extraction process economically infeasible. A proven method for enhancing the solubility of the propellant in SCF CO2 is addition of simple polar modifiers at levels as low as 1-5%. The solubilities have been shown to increase up to several hundred percent upon this small addition. We propose research to determine the optimal physical conditions and chemical makeup of an effective SCF CO2 solvent plus a polar modifier using well-established computational chemistry techniques and high performance computers. Computer simulation is an inexpensive and safe method of filtering a wide assortment of chemical systems, leading the experimentalist more quickly to successful candidate solvents. This research is coordinated with, and in support of the experimental SERDP proposal D009 submitted from our laboratory.

7. **Project Description:**

This will be a continuation of SERDP funded FY94 6.1 and FY95 6.2 research funding for FY96. The work is divided into two complementary parts that are being pursued in parallel. Part 1 explores the actual dynamical event for the first step in the SCF solvation process, i.e., the dissolution of an RDX crystal into a SCF solvent. The second part is a more rigorous quantum chemical study on the relative abilities of real modifiers to stabilize an RDX molecule in the SCF solvent.

Part 1. The simulation model will consist of an RDX crystal immersed in SCF CO2 doped with model modifier molecules (MMs). The CO2, MMs and the crystal will all be described by a purely classical potential energy function that includes hydrogen bonding, dispersion forces, and

electrostatic interactions. The description of the MMs will be flexible enough to span a wide range of both polarity and polarizability, since these are characteristics often associated with dissolution capability of a solvent. Constant pressure, constant temperature rigid body molecular dynamics simulations will provide a dynamical picture of the molecular micro-environment of the system as it dissolves, as well as indicate relative ability of each different SCF mixture to break up the lattice. This qualitative picture can lead to selection of modifiers with specific chemical and physical properties that should maximize the dissolution of RDX in the SCF solvent.

Parameters that will accurately describe the intermolecular interactions can be obtained through the use of recently developed quantum chemical techniques such as nonlocal density functional theory (NDFT)[2], second-order Moeller-Plesset (MP2) and symmetry adapted perturbation Theory (SAPT)[3,4]. The molecular structure of each compound will be determined once by doing geometry optimizations of each isolated molecule using MP2 or NDFT. These molecular structures will then remain fixed. The intermolecular interactions will be fitted to pairwise interactions between the different compounds using the SAPT method developed specifically for this task. In addition, the intermolecular interaction terms will include the ability of the partial charges, and hence the multiple moments of each molecule, to adjust to the electric field around it as the molecular dynamics proceeds.

Part 2. This part of the modelling combines quantum and classical methods to produce a more quantitative prediction of solubility by attempting to calculate the free energy of solvation, i.e., (del)F = (del)H -T(del)S, for one or more RDX molecules in SCF CO2 as a function of the specific modifier molecules included in solution. The solution space will be divided into two zones; 1) an inner "action" zone, and 2) an outer "bath" zone. The action zone will consist of an RDX molecule, the first and second solvation shells of SCF CO2, and the MMs. The action zone will be treated purely quantum chemically for the determination of changes in the enthalpy, H, using a combination of NDFT and SAPT. The action zone will be surrounded by the bath zone made up of a layer of CO2 molecules described by a classical potential energy function. This bath zone will provide boundary conditions for the quantum chemical action zone, as well as allow us to control the pressure/volume in the action zone. Such a combined quantum/classical approach has already been used to study catalysis on zeolytes[5]. The total quantum chemical energy calculated for the action zone will give the enthalpy of the (RDX + SCF CO2 + Mms) solution. This will be calculated for each of the proposed modifier compounds. The change in enthalpy, (del)H, needed as part of the free energy, can then be obtained by a thermodynamic calculation as the difference between the total enthalpy of the action zone and the sum of the enthalpies for each isolated molecules calculated at the same level of theory. The entropic term, (del)S, will be approximated by calculating the full vibrational spectrum of the action zone. The (del)S will be calculated as the difference between the sums of the vibrational energies over the action zone first with the modifier molecules included, then excluding the modifier molecules. This difference in total vibrational energies should give the contribution of the MMs to (del)S for solvation of RDX in the SCF mixture.

1. J.M Dobbs, J.M. Wong, R.J. Lahiere and K.P. Johnston,
Modification of Supercritical Fluid Phase Behavior Using Polar

Cosolvents, Ind. Eng. Chem. Res. 26, 56 (1987).
2. R.G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, N.Y. 1989.
3. T. Cwiok, B. Jeziorski, W. Kolos, R. Moszynski, and K. Szalewicz, J. Chem. Phys. 97, 7555 (1992), and references therein.
4. B. Jeziorski, R. Moszynski, A. Ratkiewicz, S. Rybak, K. Szalewicz, and H.L. Williams, in: Modern Techniques in Computational Chemistry: MOTECC-93, ed. E. Clementi, in press.
5. J. Sauer, The Combined Ab Initio and Classical Potential Approach to Zeolite Catalysis, Presented at BIOSYM Catalysis and Sorption Consortium Meeting, Parsippany, N.J., October 7, 1993.

8. Expected Payoff:

Timely development of a method for recycling solid propellants to keep the Army in compliance with EPA standards for reducing atmospheric, ground, and water pollutants. Computer modelling has been widely recognized by the chemical and pharmaceutical industries as a cost cutting technique in the pursuit of chemical properties for systems of interest to the manufacturer (see; "Promise Of Rich Payoffs Drives Computer-Aided Chemistry" in Research & Development Magazine, p. 28, September, 1993; and "The Question Is Not Whether But When To Go For Computer Aids", in Today's Chemist At Work, vol. 2, p. 20, 1993). The same cost cutting needs are obvious in today's environment of shrinking DOD budgets. Furthermore, computer modelling will reduce both the personal and environmental risks associated with experiments involving military hazardous materials.

9. Milestones/Accomplishments:

1. Procure and configure theoretical chemistry computer software — 11/94
   (a) The SAPT, NDFT and MP2 theoretical chemistry software has all been procured and is being used to perform the research.
   (b) Improvements are constantly being made on the SAPT methods by in-house researchers in parallel with its use to predict the dimer potential energy surfaces. More accurate interaction energies can now be predicted at one-fourth the computer time and storage needed by the original software.
   (c) Additional computer software has been procured to aid in this project: SEMICHEM - produces computer graphical images of complicated molecular arrangements; and ACES2 - produces highly accurate interaction energies for strongly interacting molecules, where SAPT can not be used.
2. Complete initial development of Solid RDX computer model — 03/95

(a) Through research contracted out to Oklahoma St. U. using SERDP funds, an initial empirical potential computer model has been made for crystalline RDX.
(b) Test calculations are underway to check the validity of the model by reproducing known experimental properties of solid RDX such as crystal structure, heat of sublimation, vaporization pressures, etc.

3. Complete development of action and bath zones 09/95
(a) An initial Monte Carlo model has been created for SCF CO2 using a published potential energy function. Test calculations show it reproduces some gross features of SCF CO2.
(b) Quantum Chemical calculations of the following dimer interaction energies are underway: CO2-CO2, CH3CN-CO2, dimethylnitramine-CO2. These interaction energies will be used to improve the potential energy function used in the SCF CO2 Monte Carlo calculations.
(c) Initial Quantum Chemical calculations to predict the effect of polar modifiers on the structure of RDX have been completed. More refined models are now being studied.
(d) The first computational prediction of the Infrared (IR) and RAMAN spectra of RDX have been completed, allowing for the unambiguous assignment of the observed experimental spectra. This offers a way for experimentalists to study structural changes in RDX in SCF CO2. This valuable experimental data could be fed into our model to enhance its accuracy.
(e) The IR and RAMAN spectra have been studied as a function of the dielectric strength of the polar modifier, serving the same usefulness as mentioned in (d).
4. Molecular dynamics simulation of complete system--ranking of modifier properties 03/96
5. Predict Free Energies of RDX in S/MM solvents 09/96
6. Provide database of RDX solubility vs MMs in S CO2. Use existing model to predict solubility of other propellant mixtures and/or study other S fluids besides CO2. 09/97

10. Transition Plans:

FY94 is 6.1 based research that will move to 6.2 funding in FY95, and will remain 6.2 based through FY96. During this period the theoretical chemistry models will be constructed and verified, and calculations on various model modifier/CO2 SCF solvents will begin. The results of these simulations will rank the modifiers according to their ability to increase the solubility of solid propellants in SCF CO2 and possibly other supercritical fluids. In FY97 funding

progresses into 6.3 as we provide a data base of solubilities for an array of modifiers in SCF CO2. The computer model itself can now be used as a screening device for other propellant mixtures and other modified SCF fluids besides CO2.

11. Funding: $(K)

SERDP

FY94	FY95	FY96	FY97	FY98	TOTAL
350	158	200	300	400	1,408

12. Performers:

Dr. Hayes Williams, ARMY/U.S. Army Research Laboratory, APG, MD - Improving productivity of SAPT computational method and performing dimer interaction calculations with SAPT.
Professor Krzysztof Szalewic, Departments of Chemistry and Physics, University of Delaware - Assist in studies of intermolecular interaction energies also using SAPT methods.
Professor Donald L. Thompson, Department of Chemistry, Oklahoma State University - Assist in the classical molecular dynamics simulations.
Dr. Jeffrey Morris, ARMY/US Army Research Laboratory, APG, MD - The POC for the in-house experimental research on modified SCF CO2.

13. Principal Investigators:

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14. Keywords:

Supercritical Fluid Extraction, Propellant Recycling; Solid Propellant Extraction.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non Ozone Depleting Sealants for Ammunition Applications

3. **Agency:** U.S. Army

4. **Laboratory:** U.S. Army Armament, Research, Development, and Engineering Center (ARDEC)

5. **Project ID:** #674

6. **Problem Statement:**

Goal: The goal of this program is to eliminate and replace the currently used series of ozone depleting case mouth sealants, for small and medium caliber ammunition, with environmentally safe alternatives. These materials would also be applicable for threaded and fitted material components such as fuzes.

Background: Currently, the Army, Navy, Air Force, Special Forces, and other military organizations have mandated the elimination of Ozone Depleting Chemicals (ODC's). Unfortunately, most of the military's small and medium caliber ammunition, currently in the inventory, uses solvent rich, highly toxic, ozone depleting chemicals such as 1,1,1 trichloroethane (TEC) in their sealant materials. It is essential that these materials be replaced with solvent-free or solvent-safe case mouth sealants. This is necessary because the commercial equipment and practices currently available have been found to be relatively ineffective in controlling VOC emissions.

7. **Project Description:**

Technical Objective: This research program is aimed at investigating alternate solvent-free or solvent-safe case mouth sealants for military ammunition. This will be accomplished by evaluating state-of-the-art, commercially available non ozone depleting sealants which are compatible with current production application equipment requiring little equipment modifications.

Technical Approach: Efforts will be aimed at testing and documenting the compatibility, reliability, and durability of non-ozone depleting sealants that will also meet all of the ammunition acceptance requirements. Promising candidates then will be subjected to functional testing and characterization, as well as lot acceptance evaluation. Initial selection of commercial materials will be based on a study of mechanical, chemical, and physical property data as well as manufacturers recommendations. A material specification will be prepared for best candidate alternatives.

Tasks:
- Document sealant properties relevant to ammunition applications
- Search for viable candidates
- Conduct "fast track" testing to select best candidate materials
- Conduct functional testing with best candidates
- Evaluate on line application techniques
- Document data for technology transfer

Relationship to DoD/DOE Environmental Objectives: DoD/DOE have mandated the reduction/elimination of ozone depleting chemicals from military material.

Other Work: The reduction/elimination of ozone depleting chemicals is a relatively new requirement, and similar/prior R&D efforts in this field have not been found.

Technical risks are minimal for this proposed effort.

8. Expected Payoff:

A payoff is expected in several specific areas. First and foremost is that significant amounts of sealants with ozone depleting, toxic solvents, such as 1,1,1, trichloroethane, will be eliminated; yielding a notable environmental benefit. As an example, the yearly usage of ODC sealants that would be eliminated at the Lake City Army Ammunition Plant is estimated at 2,000 gallons of 1,1,1 trichloroethane (5.56mm, 7.62mm, and .50 cal rounds) and 700 gallons of other assorted ODC solvents (20mm rounds). Economic benefits include reduced costs (elimination of toxic ODC environmental protection activities), increased production rates, reduced scrap ammunition (estimated at $2 million per year), and reduced lot rejection rate (which currently averages 6% per year). Other benefits include reduced ODC health/ safety problems, reduced misfires/hangfires, decreased damage to weapon systems/vehicles, and improved personnel safety.

9. Milestones/Accomplishments:

1. Program start	10/94
2. Prepare SOW for contractor participation	11/94
3. Procure candidate sealants	01/95
4. Contract awarded	01/95
5. Review data on candidate sealants	02/95
6. Initiate "fast track" testing	02/95
7. Solicit quotes for vendor participation	04/95
8. Contract task revision	04/95
9. Evaluate cost estimates for quality tests	10/95
10. Select best candidate(s) for on line production	02/96
11. Initiate production for quality tests	02/96
12. Interim report	04/96
13. Finalize production for quality tests	05/96

14. Initiate quality tests	05/96
15. Complete quality tests	07/96
16. Developmental material specifications	10/96
17. Generate ECP	10/96
18. Final report	12/96

Results have shown that low Volatile Organic Chemical (VOC) solvent-borne sealants and water-borne sealants offer promise as viable alternate candidate materials to replace the existing ODC and high VOC solvent-borne case mouth sealants. More specifically, water borne asphaltic resin based sealants are offering good performance and properties with the tests conducted thus far. Asphaltic based resins are most promising since they are virtually drop in replacement and have proven to be reliable, durable, and compatible with the energetic materials.

Work is now in progress to select and optimize the candidate material(s) for on line production of rounds for quality testing.

10. Transition Plan:

Acceptable materials will be commercially produced sealants that are readily available for immediate use. Project R&D personnel will be working closely with users and producers to ensure that useful needed sealants are selected and are readily available to the production arena.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	250	113	337	700

12. Performers:

The Adhesives Section of the Armament Engineering Directorate, U. S. Army Armament Research, Development and Engineering Center will perform the study, working in close coordination with industrial manufacturers/suppliers and with other government organizations: Close Combat Armament Center (CCAC), ARDEC (all rounds); Olin Corp., Lake City Army Ammunition Plant (LCAAP) (5.56mm, 7.62mm, .50 cal, M50, GPU); Ballistic Services Office (LCAAP) and TECOM (test & evaluation).

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14. Keywords:

Ozone Depleting Substances, ODC, Case Mouth Sealants, TCE

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Solventless Manufacture of Propellants Using Thermoplastic Elastomer Binder

3. **Agency:** U.S. Navy

4. **Laboratory:** Army Armaments Research, Engineering & Development Center Naval Air Warfare Center/Weapons Division Naval Surface Warfare Center/Indian Head Division

5. **Project ID:** #867

6. **Problem Statement:**

The goal of this project is to develop and evaluate artillery propellant formulations which can reduce or eliminate use of solvents containing volatile organic compounds (VOCs). The Army Single Manager for Conventional Ammunition (SMCA) has a model plant initiative for the Radford Army Ammunition Plant (AAP). The goal is to bring the polluting emissions from this plant as close to zero as practical. In 1991 the volatile air emissions from this plant average 12.5 tons per day. The SERDP project on Clean Agile Manufacturing of Energetics (CAME) is demonstrating solventless processing of thermal plastic elastomer (TPE) binders in propellants. Use of solventless process TPE propellants from the CAME SERDP project in artillery propellant will contribute to achieving the goal of the Radford model plant initiative. Further, TPE based artillery propellants can be reprocessed into other products (rather than destroyed) at the end of their useful life. This project proposes to develop and evaluate TPE based artillery propellant formulations which might be manufactured at Radford AAP for specific Army applications.

7. **Project Description:**

7.1 Technical Objective: The objective is, using TPE materials and solventless processes demonstrated in the CAME SERDP project, to measure data the Program Executive Officer for Field Artillery Systems (PEO/FAS) requires from the energetic materials community prior to evaluating or developing further new materials for specific applications.

7.2 Technical Approach: This project will measure, for specific modular charge formulations appropriate for a 155mm howitzer, burning rates at high pressure, mechanical properties at high strain rates, safety data, thermal stability, chemical properties, sensitivity, processing (rheological) properties, and pollutants produced during manufacture. The formulations will be evaluated for proof of principal testing and melt processability.

7.3 Relationship to the DoD/DOE Environmental Objective: This project is responsive to the DoD Environmental Technology Requirements Strategy, Reduce VOC's in Ordnance Manufacture.

7.4 Relationship to Similar/Related Projects: The SERDP CAME project is demonstrating solventless processing technologies using TPE binders and is quantifying their benefit, from a pollution perspective. The CAME project is not developing or evaluating formulations for specific applications. TPE solventless processing methods successfully demonstrated by the CAME project will be made ready for consideration by PEO/FAS in specific formulations (artillery propellant) for specific applications (155mm howitzer) by this joint Army and Navy project.

The Tank Main Armament System (TMAS) program office is funding a 6.1 effort to develop gun propellant formulations, including TPE based formulations. The formulations will not be produced using solventless processes. All three projects (TMAS, CAME, this proposed project) will share data.

The CRUSADER project is developing a modular charge for 155-mm howitzer ammunition using M30 propellant. This is a triple-based propellant produced at Radford using solvent. This project might provide an alternate artillery propellant which can be manufactured in a solventless process.

8. Expected Payoff:

Elimination of the use of solvents in the manufacture of artillery propellants will contribute to: (1) achieving an ordnance goal included in the DoD Environmental Technology Requirements Strategy; (2) enabling the Army to achieve the goal of its Radford model plant initiative; and (3) provide an artillery gun propellant for consideration in programs under the cognizance of PEO/FAS.

9. Milestones/Accomplishments:

FY95
Choose artillery propellant formulation
Measure sensitivity properties
Measure mechanical, chemical, and burn rate properties
Measure processing (rheological) properties

FY 96
Grain design
Gun firings

FY 97
Optimize formulation and charge design

FY98
Demonstrate propellant manufacture in a twin screw extruder such as the one at the Flexible Manufacturing Facility for Energetic Materials at the Longhorn Army Ammunition Plant or at any other plant designated by SMCA.

10. Transition Plan: Transfer technology results to:

Radford Army Ammunition Plant PEO/FAS for PALLADIN, CRUSADER, TMAS

11. Funding: $(K)

SERDP

FY96	FY97	FY98	FY99	TOTAL
250	300	300	300	1,150

Additional funding will be sought from Army sources for FY96-FY97. We have no commitment from Army sponsors at this time.

12. Performers:

Naval Air Warfare Center/Weapons Division (Tom Stephens)
Naval Surface Warfare Center/Indian Head Division (Connie Murphy)
Armaments Research, Development, and Engineering Center (Lee Harris)

13. Principal Investigator:

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14. Keywords:

Thermoplastic Elastomer Binder, Propellant, VOC's, Solventless Manufacture

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** DoD/DOE Clean Agile Manufacturing of Energetics Materials

3. **Agency:** U.S. Navy

4. **Laboratory:** Office of Naval Research (ONR)

5. **Project ID:** #63

6. **Problem Statement:**

Approximately 100 million pounds of energetic materials (propellants, explosives, and pyrotechnics (PEP)) are produced each year for DoD, DOE, and NASA as main charge explosives, solid rocket propellants, and flares/illuminators. Many are based on energetic materials that could negatively impact the environment during an item's life cycle.

Under Executive Order 12856, Federal facilities are required to achieve a 50% reduction of hazardous wastes by 1999. PEP chemicals and products are produced in government operated, GOCO, and defense contractor facilities. Ever stricter environmental regulations and waste restrictions are curtailing production of some PEP chemicals (for instance TNT). Department of Energy and NASA also have PEP waste reduction requirements.

Past waste reduction has been accomplished by cleaning up individual PEP production processes. Future waste reduction can be achieved by pollution prevention measures throughout the PEP product life-cycle. The product life-cycle includes synthesis of PEP chemicals; formulation of chemicals into a product; chemical processing, loading, and unloading of the product; combustion emissions; and methods to reclaim and recycle or reuse excess material.

7. **Project Description:**

Technical Objective: The objective of this program is to develop integrated product/process development (IPPD) technologies and tools to achieve concepts for reconfiguring existing PEP life-cycle facilities into a clean, agile enterprise that will function economically with total life-cycle wastes reduced by 90%. In the context of this proposal, life-cycle facilities are defined to be the set of existing, geographically separate, PEP facilities that design, develop or produce PEP products, recycle the production by-products into usable products, or recycle PEP parts returned as excess from the ordnance inventory. Many facilities operate under the oversight of the Army Single Manager for Conventional Ammunition.

Significant advances have been made synthesizing new PEP chemicals (e.g., TNAZ, thermal plastic elastomers). These new chemicals could enable manufacture of PEP products with significantly lower pollution. Since processes or facilities that produce and handle these new

materials have not yet been specified, designed or built, they are prime candidates for demonstration of the IPPD approach that will enable design of the clean, agile facilities that will be able to comply with future environmental regulations.

The Environmental Protection Agency (EPA) has established a Life-Cycle Assessment guidelines to evaluate environmental effects consistent with criteria established by the Society for Environmental Toxicology and Chemistry (SETAC). The DOE Office of Energy Efficiency, through its Life-Cycle Computer-Aided Data (LCAD) project, is creating software designed to integrate EPA LCA into business practices. The DOE software is being used to assist in following EPA guidelines in order to identify phases of the PEP life-cycle where considerable pollution is generated. Using experimental data generated in PEP facilities, life-cycle assessments are used to estimate if alternative materials or processes will prevent pollution.

Technical Approach: Government and industry PEP R&D labs, pilot plants, and production facilities have been organized into a program network. Laboratory, plant, and production data are used in models and simulations to predict life-cycle pollution. Pollution prevention technologies and new facility concepts will be experimentally tested in existing facilities. Facility design concepts will be developed, addressing chemical engineering unit operations, mass/energy balances, regulatory requirements, safety, pollution prevention and costs.

Life-Cycle Assessment Simulation Tool: The DOE LCAD model will be used to assess the complete pollution picture for PEP product life-cycles. LCAD models the inputs (raw materials, energy), outputs (products, by-products), and wastes (vapor, liquid, solid). A second DOE model, EcoSys, is used to evaluate the environmental impact of various product life-cycles. The simulations are validated by existing data and experiments done through the project network.

New Materials and Processes to Prevent Pollution: TNAZ is a promising new, melt castable energetic ingredient that has potential for providing environmental benefits and military performance improvement in places where melt castable TNT was used in the past. TNT is no longer manufactured in the United States for various reasons including the pollution (red water) created during its manufacture. A TNAZ manufacturing process using no chlorinated and ozone depleting solvents has been demonstrated which simultaneously increases the manufacturing yield to 75% (from the 15% yield of the previous process using chlorinated solvents). A TNAZ pilot plant which uses no chlorinated or ozone depleting solvents is being assembled in an existing California TNAZ plant. The pilot plant will be able to manufacture TNAZ is quantities sufficient to meet the needs or ordnance development programs and provide data for subsequent design of a full-scale manufacturing facility.

Thermal plastic elastomers (TPE) are desirable binders for PEP formulations because their solidification process is based on reversible, physical change (crystallization) rather than irreversible, chemical change (crosslinking). Thus, in principle, a TPE-based PEP formulation can be recovered, recycled, reused or reprocessed, thereby reducing waste generation during demilitarization. The production and reclamation of TPE-based PEP can be done using solvents in their liquid or supercritical state, thereby reducing airborne emissions. A TPE pilot plant is being assembled in an existing California binder plant. The pilot plant will be able to

manufacture TPE in quantities sufficient to meet the needs or ordnance development programs and provide data for subsequent design of a full-scale manufacturing facility.

A manufacturing process for loading explosives into small bomblets is being demonstrated which reduces the number of bomblets rejected as being inadequately loaded or loaded so as to be unsafe for use. A momentum transport problem which causes underloading of bomblets was eliminated by using smart process control to track the volumetric flow rate as a function of ram velocity and to track shear stress as a function of applied pressure. The same process control system would be used to load TPE-based PEP into munitions.

8. Expected Payoff:

This program will result in new PEP materials, processes and concepts to reconfigure existing PEP facilities to reduce hazardous wastes beyond the requirements of Executive Order 12856. The output of this project is intended to mitigate price increases for future PEP products due to cost of complying with environmental regulations. Introduction of pollution preventing materials and processes will help curtail facility shutdowns or unscheduled retirement of ordnance systems.

Utilizing the program network of existing laboratories, pilot plants, and production facilities will:
1. Preclude duplication of existing facilities;
2. Reduce construction funds needed for new plants; and
3. Allow each unit of the project network to contribute to preventing pollution in the life-cycle phase in which it is most knowledgeable.

At the end of the program, a PEP life-cycle simulation tool will be available to the Army Single Manager to assist in reducing life-cycle pollution as the PEP production base continues to be modernized. The models will produce simulations to facilitate understanding of current operations, assist in evaluating alternative processes, and quantify future environmental gains which might be achieved through clean and agile facility design.

9. Milestones/Accomplishments:

FY93

1. Technology transition plan and program network established
2. Pollution prevention product/process surveys - completed
3. Life-cycle simulations of two RDX products (PBX N109 in GBU-24 bomb and M43 propellant) - completed

FY94

1. Initial pollution prevention technology prioritization - completed
2. TNAZ synthesis improvement - completed
3. Bomblet explosive loading technique demonstrated which reduces number of rejected bomblets by a factor of five

4. EPA life-cycle inventory for GBU-24 bomb completed using LCAD
5. Life-cycle impact for GBU-24 bomb completed using EcoSys

FY95

1. A smart computer aided chemical process design tool (called Batch Design Kit) is applied to PEP process which allows chemists and engineers to select batch processes that achieve a balance between production costs and waste emissions
2. Demonstrated separation of RDX from TPE in a laboratory environment

To be achieved with FY96-97 SERDP funds:

1. Completion of TNAZ pilot plant and experimental verification of waste reduction
2. Completion of TPE pilot plant and experimental verification of waste reduction
3. Demonstration of bomblet process control method which reduces bomblets rejected for poor loading quality by 90% from the 1994/95 reject rate
4. Batch Design Kit is completed for PEP processes
5. LCA software use is estimate life-cycle waste reduction relative to 1992 baseline
6. LCA simulation software becomes available for Army Single Manager through the Army Production Modernization Activity at Picatinny Arsenal

We have completed most of the FY94 milestones by demonstrating two items. First, scale-up of a cleaner process for manufacturing the melt castable explosive called TNAZ to 20 kilograms (45 pounds) batches. This process eliminates the use of chlorinated solvents during manufacture of TNAZ. The new process has a higher yield than the process it replaces (75% compared to 15%). Second, demonstration of injection loading as a cleaner process for loading PBX N-107 explosive into BLU-97 submunitions used by the Joint Stand-Off Weapon and Tomahawk cruise missile. The rejection rate is reduced form about 24% to about 5%. The new process reduces the need to dispose of scrap as it reduces the consumption of VOC solvents used in manufacture.

10. Transition Plan:

The beneficiaries of this program are existing development, production and reclamation facilities operated for the Army Single Manager and DOE, GOCOs and commercial industry. Introduction of the new PEP chemicals and processes into the existing facilities will contribute to achieving ordnance pollution prevention objectives.

11. Funding: $(K)

SERDP

FY93	FY94	FY95	FY96	FY97	TOTAL
2,000	3,700	600	2,500	1,100	9,700

12. Performers:

This project will be jointly managed by DoD and DOE. The Program Manager resides at the Office of Naval Research. The performers in the program network will include DoD ordnance laboratories (e.g., Naval Surface Warfare Center, Indian Head Division, Naval Air Warfare Center/Weapons Directorate, Army Research Development Engineering Center, Production Base Modernization Activity), DOE National Laboratories (Los Alamos, Lawrence Livermore, Sandia), Army Ammunition Plants (Holston, McAlester), industry R&D labs (Thiokol, Aerojet), universities (Cal Tech, MIT, New Mexico Tech, Stevens Institute of Technology, University of North Carolina, University of Rhode Island), university consortia (Emission Reduction Research Center at the New Jersey Institute of Technology) and small businesses (Strategic Analysis).

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14. Keywords:

Propellants, Explosives, Pyrotechnics, Environmental Life-Cycle Assessment, Pollution Prevention, TNAZ, Thermal Plastic Elastomer

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Pollution Prevention Enhancement

At time of printing no information was available on this project.

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Solventless Pyrotechnic Manufacturing

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Surface Warfare Center, Crane Division (NSWC, Crane)

5. **Project ID:** #757

6. **Problem Statement:**

Because the manufacturing use of volatile organic compounds (VOC)'s as processing solvents is a major source of the nation's pollutant waste streams, it is important to modify or replace processes in order to minimize or eliminate the use of VOC's. In our work we will focus on processes for manufacturing energetic materials that are concerned with pyrotechnic materials that are used, for example, as grain materials for air-countermeasures (infra-red decoys) and as igniters in Jet Assisted Take Off (JATO) and tactical rocket motors. These devices play major roles in certain defense areas, infra-red decoys being critical in the countermeasures suites deployed on tactical aircraft, while tactical rocket motors find important air defense and air-to-air interception applications.

The majority of these pyrotechnic compositions are currently manufactured using a crash precipitation method called the "shock-gel" process. The process generates large amounts of hazardous waste and constantly releases VOC's and toxic air pollutants (TAP's) to the environment. In the case of magnesium-Teflon-Viton (MTV), one such pyrotechnic used for solid rocket igniters, 1 lb of material generates from 0.3 to 1.5 gallons of waste solvent, depending on the processing facility.

Increasingly stringent environmental legislation, such as, the Clean Air Act Amendments of 1990, are increasing the manufacturing costs of these critical pyrotechnics by forcing the producers to reduce the hazardous air emissions and minimize the waste generated. Pollution abatement techniques alone will not be adequate to satisfy those restrictions. The obvious solution is to eliminate the solvents from the production process.

The Solventless Pyrotechnic Manufacturing project is aimed at eliminating all the hazardous solvents and associated emissions from current and future pyrotechnic formulations used in these critical applications. This 6.2/6.3 research will be performed concurrently at two separate divisions of the Naval Surface Warfare Center. Each division has unique expertise, facilities and equipment which will ensure success of the project.

The program is a combination of two separate efforts and as such would be composed of two phases. The first phase of the program would demonstrate a solventless cryogenic production process for the manufacture of MTV. This phase of the project would be a continuation of previous SERDP work (under the same title) which dealt solely with cryogenic processing of MTV and the installation of a pilot scale facility at the Indian Head Division. The second phase would develop castable pyrotechnic formulations based on modern polymeric binder systems. This phase of the project would be a follow on to the previously funded work and would be directed toward the modification of a decoy composition now under development and toward appropriately modifying the in-service composition to make it castable. Currently the developmental work being conducted at the Crane Division is funded under a NAVAIR air-countermeasures PIP program and on ONR Electronic Warfare (Infrared Countermeasures) 6.2 research program.

Both phases of the proposed work are complemented by similar efforts from U.S. Army Armament Research, Development and Engineering Center (ARDEC). In the cryogenic phase ARDEC is investigating the cryogenic processing of magnesium-Teflon-Hytemp (MTH) pyrotechnics. A joint effort in 1989 between the Indian Head Division and ARDEC resulted in two separate areas of investigation each focused on resolving the unique processing difficulties of each binder system. In the castable pyrotechnic phase ARDEC is developing a modification of the decoy composition as part of an ARMY AIRCMM project.

7. Project Description:

The objective of the Solventless Pyrotechnic Manufacturing project is to demonstrate two alternative approaches as methods of eliminating the hazardous waste and VOC emissions caused by the solvents used in the manufacture of MTV and similar pyrotechnic materials. Both the phase 1 cryogenic approach and the phase 2 castable pyrotechnic approach offer unique solutions to the pollution problems associated with the current solvent manufacturing process. Once both phases are completed they will provide the Navy and other DoD facilities with a full spectrum method to eliminate solvents and prevent VOC emissions from inservice and future pyrotechnic formulations. The project is listed under heading 3C5 of the Tri-Service Environmental R&D Strategic Plan (Green Book).

The cryogenic process for manufacturing MTV is a solventless process that has been demonstrated on a small scale. In the cryogenic process the Viton is cryogenically ground to a fine particle size using inert liquid nitrogen (LIN). Magnesium and Teflon are then chilled to LIN temperatures. Once the ingredients have reached equilibrium, they are mixed in a slurry of ground Viton and LIN. When a uniform distribution of the ingredients has been attained the temperature of the slurry is increased and the LIN is vaporized. Once the LIN has vaporized, the relatively free flowing pyrotechnic powder can be pressed or extruded into the appropriate size and shape using conventional molding technology. In terms of environmental liabilities, there are none. Nitrogen is an environmentally benign gas that makes up 79% of the air we breathe every day. Upon completion of Phase 1, the Navy will have a pilot plant capable of manufacturing solventless MTV and investigating other pyrotechnic applications.

The second phase of this project will use modern polymeric binder materials to formulate pyrotechnic compositions emphasizing their use for castable grains for decoy devices. Rocket composition formulating has driven the development of curable polymeric materials for application in energetic composites. We propose to formulate candidate pyrotechnic flare materials that employ binders of this type. The major technical challenge will be to find binder material that will cure to give pyrotechnic grains that perform in their decoy function as required. We feel that there is great potential for application in developmental composition system of binder material candidates from the general class of azide-containing, curable pre-polymers. These binder materials are currently available in limited commercial quantities from at least two manufactures.

Major tasks to be carried out in phase 2 include material procurement, laboratory scale formulating, functional testing, scale-up and performance testing. Some of the laboratory scale formulating and functional testing has already begun. Most performance testing will be carried out at the Crane Division using facilities and equipment elaborated specifically for the ground-based testing needed in their decoy development.

8. Expected Payoff:

Solventless pyrotechnic manufacturing will result in an environmentally compliant process which is safer and less costly than the current solvent manufacturing process. Both the cryogenic and the castable pyrotechnic processing approaches can eliminate the large quantities of hazardous solvent waste and VOC emissions currently generated in production. The elimination of waste streams from any process eliminates the need to install expensive solvent recover and recycling systems which will require additional energy usage, constant maintenance and possible upgrades to remain in compliance as regulators lower discharge thresholds.

The potential payoff in terms of hazardous waste elimination can be readily estimated from procurement figures for FY95. The Navy is planning on procuring some 100,000 lbs of flare decoy composition, the Army about half that and the Air Force approximately 5 times that of the Navy, totalling 650,000 lbs per year. This estimate only represents one family of decoy compositions, however, this amount of material will generate anywhere from 195,000 to 975,000 gallons of hazardous waste solvent. The current cost of disposing of waste solvent at the Indian Head Division is 600 dollars per 55 gallon drum. Based on this figure the total cost savings from the solvent elimination alone is anywhere from 2.1 to 10.6 million dollars. When everything is considered such as procurement costs of alternative materials these numbers are probably high.

Based on the cryogenic approach, the Army has estimated a potential cost saving of $900,000.00 if their current 600,000 lbs per year "shock-gel" production process for flare decoys were replaced with the cryogenic process. The cost savings realized from not installing solvent reclamation and recovery systems have not been included.

9. Milestones/Accomplishments:

Phase I Milestones -

1. Procure ingredient precoolers and feeders*	07/95
2. Grind viton on pilot scale	01/95
3. Procure large scale cryogenic mixing vessel*	12/94
4. Manufacture small scale MTV mixes	05/95
5. Extrude and test MTV	06/95
6. Benefit/cost analysis of a multiple mill grinding system	11/95
7. Prepare final report, Phase I	12/95
8. Install granulator for optical analyzer	04/95

Phase II Milestones -

1. Complete lab work-up for GAP-based comp's	01/95
2. Complete scale-up to 2lb batches of GAP-based compositions	05/95
3. Complete function testing of material, 2lb batches GAP-based	09/95
4. Complete lab-scale work, gray-body illuminant	09/96
5. Select castable (gray body decoy system) for scale-up	11/96
6. Complete preparation of materials for full size grain testing	09/97
7. Complete ground-based performance testing	06/98

* The emphasis of the Phase I cryogenic processing tasked changed from demonstration of continuous production to demonstration of batch-wise processing on a pilot scale, with determination of the processing parameters needed for continuous production. For this reason, milestones 1 and 3, although actually completed, became superfluous for the SERDP project. Few or no SERDP funds were actually expended to complete these milestones.

The Phase I part of the project is complete, except for submission of the final report, to be made in February, 1996. The goals of Phase I were modified significantly during the course of executing the project. Essentially, the original goal of making a straight-forward production demonstration on a pilot-plant scale was changed to using a pilot-scale operation, not necessarily a small scale emulation of a production operation, for establishing parameters that will be needed in the full design of an actual production operation. In fact, the ratio of production scale to pilot scale is approximately 50:1, and as such, the current equipment could not be used for production. Also, a benefit/cost analysis was performed that shows approximately a 20% cost advantage over the conventional processing method. This information will now be used to pursue sponsorship for an actual production demonstration, probably as a MANTECH project.

In Phase II, the use of the solventless cast/cure methods has been successfully demonstrated for the fabrication of special purpose decoy flares, based on the energetic binder GAP (see milestone 2 and 3 above). SERDP funding was also used to perform significant laboratory work on modifications of the GAP-based materials whose performance may better address Navy needs. A transition has effectively been carried out, as work on these materials continues as a Process

Improvement Project, sponsored by NAVAIR (PMA-222). Our communications with the NAVAIR PMA-222 technical representative during the course of the project have led to the expression of great interest on the part of that office in the possibility of a cast/cure replacement for the in-service decoy flare materials, indicating a strong possibility for sponsorship of a transition, if a suitable material can be formulated (milestone 4).

10. Transition Plan:

The transition plan for first phase transition of the project cryogenic process expected to occur at the end of FY95 and the second phase will deal with the transition of the castable pyrotechnic technology. We expect that the Indian Head Division will convert their MTV igniter production to the new process having proofed the technology in MK 22 igniter systems. Their low production requirement will enable the Navy to use the equipment as a test bed to investigate other applications for cryogenic pyrotechnic manufacture. Transition of the second phase to advanced development will take place concurrently with flight testing or after initial flight testing of the candidate decoy device occurs at the Crane Division. The funding for this transition is expected to come from a product improvement program for a particular (in-service) decoy device. It is hoped that new pyrotechnic materials developed in this phase of the project will be selected as candidates for the Navy's Advanced Technology Expendables and Dispenser System (ATEDS) program which is seeking to improve the current in service decoy device configurations.

11. Funding: $(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	355	500	113	100	300	1,408
NAVY	0	270	230	198	325	1,178
TOTAL	355	770	343	298	625	2,586

12. Performers:

The major performer for the castable pyrotechnic (phase 2) approach as well as the SERDP program management is the Naval Surface Warfare Center Crane Division. The cryogenic (phase 1) process development work will be performed by the Naval Surface Warfare Center Indian Head Division.

13. Principal Investigator:

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14. Keywords:

Pyrotechnics, Flares, Binders, Hazardous Waste Minimization, Solventless Manufacture

SERDP FY96 PROJECT

1. SERDP Thrust Area: Pollution Prevention

2. Title: Encapsulated Micron Aerosol Fire Suppression Technology

3. Agency: U.S. Air Force

4. Laboratory: Wright Laboratory (WL/FIVCF, Tyndall AFB, Florida)

5. Project ID: #113

6. Problem Statement:

This project seeks to develop and test a new fire suppression concept leverage on Soviet aerosol technology for use in a wide variety of facility and aircraft protection roles. Halons, while powerful fire suppressants, cause ozone depletion and are being eliminated. Halon 1301 replacements candidates identified this far are 2-3 times less effective than Halon 1301 in fore suppression efficiency. Known replacement agents would require major modifications to piping nozzles, and other components of the delivery systems. Suitable replacement resulting from existing programs and technologies are not available or projected to be available in the near term. A class of environmentally safe agents that can fulfill some of these fire suppression roles is badly needed and required to maintain the operational readiness and capability of the Air Force. Encapsulated Micron Aerosol Agents (EMAA) may provide the Air Force with an environmentally and occupationally safe agent that has 6 times the fire suppression capability of Halon 1301 by weight. It requires no piping or pressure cylinders and will be a fraction of the cost of Halon 1301 in installation and life cycle costs. It also allows delivery strategies other than total flood and can placed locally in high fire risk locations within a facility. FY96/97 SERDP funding will be used to continue a program initiated with FY93 SERDP and USAF funds.

7. Project Description:

Various EMAA formulations will be tested for fire suppression efficiency, materials compatibility, storage stability and lifetime, packaging, toxicity, electrical conductivity, corrosion, and combustion products. The results of these analyses will be utilized in the engineering of delivery systems for both total-flood and local fire suppression strategies. Several delivery packages and methods containing both non-electrical and electrical initiation will be designed, fabricated, and tested to determine the best practical methods for delivering fire suppression aerosols. Ultimately, large scale testing against scenario fires will be conducted to determine the final configuration of EMAA delivery systems. A CRADA with Spectrex, Inc. Will result in the basic aerosol compositions and chemistry being assessed. Applications for EMAA will center around local delivery systems that can be used without the need to resort to a total flooding of the space being protected. Possible strategies include placing an EMAA device directly in equipment that is a potential source of fire. The risks of this program are moderate. The major difficulties are the corrosion potential of the EMAA solids in a humid atmosphere, toxicological

effects of lung penetration of the micron and submicron sized particles, and the handling of high temperatures and energy developed in the creation of the aerosol. The technical program addresses each of these areas and provides for detailed analysis of each of these potential problem areas.

Tie to Tri-Service Environmental Quality R&D Strategic Plan
Pillar Thrust Area: 3.H
Requirements Category: II.4
Work Effort: Tech Demo

8. Expected Payoff:

The successful development of pyrotechnically generated aerosols as envisioned in this program will provide the Air Force with a badly needed option in the drive to replace Halon 1301 with non-ozone depleting fire suppressants. In addition to removing the threat of an environmentally unacceptable chemical, EMAA actually provides superior performance on a weight and volume basis. The results will be new applications such as fire protection systems that can easily be built into deployable shelters, hand thrown and remotely launched devices that can be used to provide "first-aid" to begin the process of extinguishment, and the potential to protect large fuel storage tanks from destruction via compact fire suppression systems. The Air Force also stands to benefit economically from the development of EMAA application because the provisions of the CRADA call for royalties to be paid to the Air Force for products created and sold as a result of the Air Force research and development investment.

9. Milestones/Accomplishments:

1. Selection of aerosol formulations	03/94
2. Particle characterization	08/94
3. Extinguishment mechanisms	10/94
4. Completion of corrosion studies	06/94
5. Thermal characterization	11/94
6. Ignition methods	11/94
7. Energy absorption methods	09/94
8. Fire suppression effectiveness	12/94
9. Toxicity testing	12/94
10. Stability testing	06/95
11. Hand thrown device testing	05/95
12. Passivelt activated device	10/95
13. Gelled aerosol technology evaluation	04/96
14. Gelled aerosol delivery system design	09/96
15. Facility delivery system design	12/96
16. Medium scale facility delivery system testing	03/97
17. Large scale facility delivery system testing	07/97
18. Final report	10/97

A first generation handthrown device was designed, fabricated and tested to determine performance characteristics. Refined design to drastically reduce high temperatures during aerosol generation thereby increasing uniformity of dispersion and reducing stratification effects. Designed and tested and the first passively ignited delivery system. Aerosol exit temperatures were reduced from 2000 deg F to about 140 deg F. Additional testing of the passive system combined with the solid pebble bed cooling system is being conducted to optimize the weight of the overall delivery system. Technology transfer efforts are underway and the Gulf Coast Alliance for Technology Transfer (GCATT) has started to display and market the aerosol fire suppression technology at trade shows and through various media.

Published refereed paper: Kibert, Charles J. And D. Dierdorf, "Aerosol Fire Suppressants," Fire Technology, 30(4). Fourth Quarter 1994, 387-399. Paper resulted in authors being selected as recipients of the 1994 Harry C. Bigglestone Award for Excellence in Communication of Fire Protection Concepts. The award included (1) a cash prize from the National Fire Protection Foundation of $1000 which was presented to the authors at the 1995 NFPA Annual Meeting in Denver CO on May 22-25 and (2) an invitation to present a paper on the work to the NFPA Research Section at the same meeting.

10. Transition Plan:

A CRADA merges the efforts of Air Force laboratories with Spectrex, Inc. To produce a powerful yet low cost fire protection system. Provisions in the CRADA create device that are suitable for Air Force application and create a licensing scheme that will allow multiple source commercialization of the end products. The CRADA requires that the Air Force receive royalties that, if the project is fully successful, will more than recover the development investment of the Air Force.

11. Funding: $(K)

	FY95	FY96	FY97	TOTAL
SERDP	284	247	740	2,551

12. Performers:

This project will be managed by the Air Base Fire Protection and Crash Rescue Systems Section (WL/FIVCF), Wright Laboratory, at Tyndall Air Force Base, FL. Extensive coordination and cooperation will be accomplished with Spectrex, Inc. Spectrex will handle issues of agent composition whereas WL/FIVCF is responsible for technical issues such as corrosion assessment, initial toxicological assessment, particle size measurements, thermal characterization, thermal absorption studies, calorimetry, and applications engineering. Several contractors will be utilized to accomplish the tasks under this effort to include Applied Research Associates (ARA), the New Mexico Engineering Research Institute (NMERI), the University of Massachusetts (Lowell), and the University of Florida. Extensive coordination will be conducted with the Army, Navy, and the FAA due to their interest in possibly utilizing this technology for their own purposes.

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14. Keyword:

Halon 1301, Encapsulated Micron Aerosol, Fire Suppressants, Ozone Depleting Substances, HCFCs, Aerosols, Solid Particulate Aerosols

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives

3. **Agency:** U.S. Army

4. **Laboratory:** Army Research Laboratory (ARL)

5. **Project ID:** #682

6. **Problem Statement:**

The presently used Halons 1301 and 1211 fire extinguishing agents are being phased out due to their role in the catalytic destruction of the stratospheric ozone layer. There is presently a major effort underway within the DoD to find environmentally acceptable Halon replacement compounds. The goal of this research project is to develop a detailed flame chemistry computer model which will be able to predict the relative flame extinguishment properties of new Halon alternative compounds as well as to identify the possible formation of toxic flame products resulting from the use of the agent. This model, once fully verified, will become a very important predictive and cost-saving tool for the RDT&E survivability laboratories for screening new compounds, or mixtures of compounds, and for interpreting results of full-scale testing. This project is a 6.2/6.3a effort since it uses information and data generated from previous basic research in flame inhibition science. It is transitioning into 6.3a as the models are simplified to include the important overall reactions. Ultimately, these reduced/simplified flame chemistry models are expected to be run on advanced PCs, rather than on the workstations which are presently required for running the full chemistry. The part of this project that covers the near-ir tunable diode laser (TDL) spectroscopy development represents 6.3a work with the intention of transferring this instrumentation technology to the DoD's real-scale testing facilities.

7. **Project Description:**

This project continues our very successful state-of-the-art approach which is aimed towards identifying the detailed chemical and physical mechanisms which are responsible for flame extinguishment. This approach consists of an experimental flame program closely coupled with various types of computational modeling efforts. This project has been particularly prolific with a large number of manuscripts having been published or in the process of being published. This includes a book on Halon Replacements: Technology and Science as well as open literature publications.

We are in the middle of transitioning from our previous work on low pressure premixed flames to our current work on counterflow diffusion burners. We are still using the Tunable Diode Laser Absorption Spectroscopy (TDLAS) technique for flame profile studies. The detailed

chemical flame mechanisms are tested on the basis of agreement with the experimental results. The modeling work typically involves on the order of a thousand elementary chemical reactions as well as nearly 100 flame species. Due to the magnitude of the required computations, this work is typically performed on workstations or larger computers. However, after the complete reaction set is verified, then the number of reactions can be significantly reduced through the use of sensitivity analysis. The detailed kinetic models are based on accurate knowledge of thermodynamic and kinetic properties of the relevant species and reactions. For those reactions where previous data does not exist, an estimate has to be determined through the use of computational chemistry tools such as the BAC-MP4 and Transition State Theory programs.

Significant progress continues to be made in both experiments and modeling. We have already obtained a large number of flame structure profiles for methane/oxygen flames doped with various perfluorocarbon (PFC), hydrofluorocarbon (HFC), and iodofluorocarbon (IFC) compounds as well as Halon 1301. Detailed chemistry flame models have been run at 20 Torr for various PFC and HFC compounds at a number of concentrations. Flame model calculations include both freely propagating flames and burner stabilized flames.

Our work has been moving continuously from the more basic research aspects to the more applied work for some time. Besides initiating diffusion flame research, which will give us very important information concerning the interplay between flame kinetics and transport processes, we have also directed our modeling toward the practical application of trying to minimize acid gas (HF) formation for new replacement compounds. In addition, we are exploring a new TDLAS technology based on room temperature near-infrared tunable diode lasers which hold great promise for in-situ and real-time detection of acid gases in large scale testing.

Strat Plan Area: 3.H Fire Fighting Agents

8. Expected Payoff:

The successful execution of this research program will benefit all organizations concerned with survivability of military platforms involved in a fire scenario. The DoD organizations working in this area include TARDEC, ATCOM, Wright-Pat, and NRL. Flame chemistry models that include fluorine, bromine, as well as iodine chemistry will be particularly useful as screening tools for a wide range of candidate fire extinguishing agents, thus leading to significant savings by avoiding unnecessary large-scale testing.

9. Milestones/Accomplishments:

1. Apply new near-infrared tunable diode laser technology for detection of HF in flames.	11/95
2. Complete low-pressure premixed flame structure studies of PFC and HFC flames	12/95
3. Complete detailed kinetic modeling of PFC and HFC flames	12/95
4. Complete modeling simulations of HF toxic gas formation	01/96

5. Complete experimental studies and kinetic data base development to include iodine and bromine reactions, work performed at NIST	03/96
6. Complete counter-flow diffusion flame structure experimental studies of PFC, HFC, and IFC flames	06/96
7. Complete detailed kinetic modeling studies of counter-flow diffusion flames	08/96
8. Final documentation of research results	09/96

Our research accomplishments take the usual form of open literature, meetings, and other technical reports. These include the following-

1. Book- "Halon Replacements: Technology and Science", A.W. Miziolek and W. Tsang, eds., ACS Symposium Series 611, American Chemical Society, Washington, DC, 1995.

2. K.L. McNesby, R.G. Daniel, J.B. Morris, and A.W. Miziolek, "Tomographic Analysis of CO Absorption in a Low Pressure Flame", Appl. Opt., Vol. 34, p. 3318, 1995.

3. A.W. Miziolek, W. Tsang, and J.T. Herron, "Halon Replacements: An Overview", Book Chapter in 'Halon Replacements: Technology and Science', A.W. Miziolek and W. Tsang, eds., p. 1, ACS Symposium Series 611, American Chemical Society, Washington, DC, 1995.

4. V.I. Babushok, D.R.F. Burgess, Jr., W. Tsang, and A.W. Miziolek, "Simulation Studies on the Effects of Flame Retardants on Combustion Processes in a Plug Reactor", Book Chapter in 'Halon Replacements: Technology and Science', A.W. Miziolek and W. Tsang, eds., p. 275, ACS Symposium Series 611, American Chemical Society, Washington, DC, 1995.

5. K.L. McNesby, R.G. Daniel, A.W. Miziolek, V.I. Babushok, S. Cheskis, and A. Amirav, "Velocity Measurements of Inhibited Methane/Oxygen Flames Using Pulsed Flame Velocimetry", Proceedings of the ASME Heat Transfer Division, Vol. 2, p. 3, American Society of Mechanical Engineers, New York, NY, 1995.

6. R.G. Daniel, K.L. McNesby, and A.W. Miziolek, "Tunable Diode Laser Diagnostics of Combustion Species", Proceedings of the ASME Heat Transfer Division, Vol. 2, p. 13, American Society of Mechanical Engineers, New York, NY 1995.

7. K.L. McNesby, R.G. Daniel, J.M. Widder, and A.W. Miziolek, "Spectroscopic Investigation of Atmospheric Pressure Counterflow

Diffusion Flames Inhibited by Halons and Their Alternatives", Appl. Spectrosc. (in press- Jan 1996).

8. R.G. Daniel, K.L. McNesby, and A.W. Miziolek, "Tunable Diode Laser Diagnostics of Halon Replacement Agents and Other Combustion Species", Proceedings of the 1995 Halon Options Technical Working Conference, pp. 275-286, New Mexico Engineering Research Institute, Albuquerque, New Mexico, May 1995.

9. K.L. McNesby, R.G. Daniel, A.W. Miziolek, S. Cheskis, and A. Amirav, "Flame Velocity Measurements of Inhibited Methane/Oxygen Flames Using Pulsed Flame Velocimetry", Proceedings of the 1995 Halon Options Technical Working Conference, pp. 541-552, New Mexico Engineering Research Institute, Albuquerque, New Mexico, May 1995.

10. V. Babushok, D.F.R. Burgess, Jr., G. Linteris, W. Tsang, and A.W. Miziolek, "Modeling of Hydrogen Fluoride Formation from Flame Suppressants During Combustion", Proceedings of the 1995 Halon Options Technical Working Conference, pp. 239-250, New Mexico Engineering Research Institute, Albuquerque, New Mexico, May 1995.

10. Transition Plan:

This research continues to be closely coordinated with the survivability organization (TARDEC, Wright-Pat, NRL, others) and the work is coupled with these organizations as our models are developed to predict large-scale testing of individual as well as mixtures of agents. As an example, we have focussed some of our attention towards the agents FE13 and FM200, which are prime candidate replacement compounds of special interest to the Army. Also, we have been working with the Army's T&E fire safety group at the Aberdeen Test Center (ATC) for some time on various issues related to flame extinction, environmental acceptability, and new instrumentation for full-scale testing. As the reduced chemistry computer combustion models are successfully developed so they can be run on advanced PCs, we will transfer this technology to the T&E communities.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	400	203	248	851

12. Performers:

The lead organization and principal performer of this project is the Ignition and Combustion Branch, Propulsion and Flight Division, Weapons Technology Directorate (formerly BRL), Army Research Laboratory, at Aberdeen Proving Ground. The work at ARL consists of expanding the flame structure studies and flame extinguishment modeling into diffusion flames. The work at NIST is fully integrated into the ARL work and consist of flame kinetic data base development and kinetic modeling.

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14. Keywords:

Halons, Fire Extinguishment, Flame Modeling, Chemical Mechanisms, Vehicle Survivability, Flame Research

SERDP FY96 PROJECT

1. SERDP Thrust Area: Pollution Prevention

2. Title: Chemistry of Halon Substitutes

3. Agency: U.S. Army

4. Laboratory: U.S. Army Research Laboratory

5. Project ID: #666

6. Problem Statement:

The goal is to identify the potential halon replacement agents which are efficient in extinguishing fuel fires without producing excessive amounts of toxic by-products. The cost, space, and weight claims of agents will be considered in assessing efficiency.

While Halon 1301 has been universally accepted as a nontoxic fire-extinguishing agent, certain toxic agents (HF and Hbr) are produced when Halon 1301 is used to extinguish flames. The amounts of these acids are generally low enough to be considered merely a nuisance. However, in studies that the Army has conducted using Halon 1310 to extinguish crew compartment fires (mist fireball explosions), the acids have been analyzed in higher than acceptable concentrations. Potential halon replacements may well be less chemically effective than the halons. It is possible that even higher quantities of toxic gases may be produced from these materials than are produced from the halons. This information should be available before expensive full-scale vehicle tests are conducted.

7. Project Description:

Previous Efforts: Private industry initiated a program to identify acceptable substitutes for the halons. Industry's criteria of acceptability is somewhat different than the Army's. The severe space and weight constraints found in fielded combat vehicles, as well as the mist fireball explosion scenario, are Army problems not addressed by industry. The Army's program addressing fire protection for engine compartments does not have the severe toxicity limitations that must be applied to normally occupied (crew) compartments. Likewise, the Air Force projects to find halon replacements for engine necell fires do not have the toxic gas production limitation that Army crew compartment fires have. The Navy is addressing the occupied volume fire problem, but no the mist fireball explosion problems.

Technical Objective: Identification of fire-extinguishing agents that will be useful in controlling fires in Army combat vehicles. These agents must be non-ozone-depleting, have minimal toxicity as unreacted chemicals, and have minimal weight and space impacts on the vehicles. Any toxic

gases formed during the fire-extinguishing process must be at acceptable levels for use of the agents in engine compartments and even lower levels for use in crew compartments.

Technical Approach: Non-ozone-depleting candidates for extinguishing agents will be studies for their ability to extinguish JP-8 fuel fires. The study will be conducted in two chambers whose interior volumes are sufficiently different to allow agent rankings based on fire size and volume of enclosure. A comparison of the amounts required to extinguish various size JP-8 fire will be made for different agents. Analyses of gases inside the chamber will be conducted to rank agents on the basis of toxic gases and carbon monoxide produced during extinguishment.

Relationship to Department of Defense (DoD) Environmental Objectives: Removal of Halon 1301 from Army combat vehicle is a DoD requirement. Any replacement agent must be a non-ozone depleter. Identification of suitable replacement agents will contribute useful information to test programs for qualifying new agents for use in occupied and unoccupied compartments of military vehicles.

Relationship to Other On-going Work: The Navy and Air Force have active halon replacement programs. Several members of the Halon Alternatives Research Corporation (HARC) have active programs in this area. Information gained is being shared with others interested in the halon replacement program.

Tasks/Activities: Input from the Army's 6.1 program and consultation with other DoD and private industry are being used to identify potential replacement agents for testing in a generic system. Agents are being ranked according to their ability to extinguish various-sized JP-8 fuel fires. Analyses of gases produced during the extinguishment process are being carried out. Another ranking of agents will be made according to toxic gas production. An overall ranking of potentially useable agents will be made and the information disseminated to interested parties.

Technical Issues to Overcome: The halons are very efficient fire-extinguishing agents because they contain bromine. But it is the bromine which causes the halon to have ozone depletion potential problems. Replacement agents identified thus far do not contain bromine. Therefore, they are less efficient than the halons. This probably translates to extra volume of agents required for fire protection. It is very difficult to find any extra storage room on a fielded combat vehicle. An agent with a lower efficiency than halon may produce more toxic gases during fire-extinguishing scenarios due to longer time in the flame zone. Toxic gases can be a major problem in crew compartments.

8. Expected Payoff:

Potential Users: Both DoD and private industry would welcome a non-ozone-depleting, low-cost, efficient fire extinguishing agent with acceptable toxic gas production. There is potential payoff for all of DoD and the world in general.

Impact: The removal of halon from combat vehicles must be carried out independent of cost considerations. The identification of acceptable replacement agents at low cost would be very

beneficial. The quicker the changeover from halon to a new agent in our combat vehicles, the better from an environmental point of view. There will be fewer accidental discharges of halon if it is removed quickly.

9. Milestones/Accomplishments:

1. Program start	10/94
2. Literature update	01/95
3. 95-liter box built	01/95
4. Analytical techniques proved for analysis of HF	11/94
5. Analytical techniques proved for analysis of HBr and HI	12/94
6. Instrumentation in place for analysis of carbon monoxide and carbon dioxide	12/94
7. Initial tests of sprays from water-based agents	03/95
8. 283 liter chamber built	08/95
9. Five agents tested with two nozzle sizes	12/95
10. Evaluation of sprays completed	06/95
11. Evaluation of mists completed	08/96
12. Interim report comparing mists and sprays	09/96

Analytical techniques that allow analysis of the acid gases (HF, Hbr, and HI) using specific ion electrodes have been developed. Using proper care, there is little interference of one halogen ion in the analysis of another halogen ion. While these techniques require extreme care, they are not as time-consuming as gravimetric techniques.

When using water-based sprays containing organic salts, it was found, as expected, that carbon monoxide was the main toxic gas produced during the extinguishment process. However, the carbon monoxide level did not appear to be at a dangerous level.

In regard to the halogenated extinguishing agents that produce acid gases, the time required to extinguish the fire was important. Using a small nozzle, the rate of delivery of extinguishment agent was low. This led to a long fire-out time and high levels of acid gas production. It is important to get the fire extinguished in a short time to keep acid gas production low.

10. Transition Plan:

Transfer: The US Army Test and Evaluation Command (TECOM), which is responsible for the testing of the US Army Tank-Automotive Command's (TACOM) vehicles, is being kept informed continuously of our results in testing new agents. TECOM will be responsible for vehicle testing for the most promising agents. Members of HARC will be informed of our results through regular HARC technical committee meetings.

Coordination: TECOM, TACOM, the Navy, and the Air Force are being continuously informed. The Navy and the Air Force will share all information with the Army to solve this common halon replacement problem.

11. Funding: $(K)

	FY94	FY95	FY96	TOTAL
SERDP	155	200	165	520

12. Performers:

In-house work will be performed at the Army Research Laboratory/Weapons Technology Directorate (ARL/WTD), Aberdeen Proving Ground (APG), MD. Involvement by universities, a nonprofit research institute, and industry will be determined from an Army Research Office (ARO) study of potential partners.

13. Principal Investigator:

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14. Keywords:

Halons, Fire Extinguishment, JP-8 Fuel Fires, Flame Chemistry Model, Flame Research, Toxic Gases, Crew Compartment Fires

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Advanced Streaming Agent

3. **Agency:** U.S. Air Force

4. **Laboratory:** Wright Laboratory (WL)

5. **Project ID:** #158

6. **Problem Statement:**

Although extensive research has been conducted by both industry and the Department of Defense (DoD), a suitable replacement for Halon 1211 used in flightline and aircraft portable fire extinguishers has not been found/developed. Prior efforts to find a replacement concentrated on currently in-production chemicals and were directed at finding a chemical that had a low toxicity, and had a fire suppressant effectiveness close to that of Halon 1211. Extensive research and testing efforts by the Air Force's Wright Laboratory (WL/FIVCF) identified perfluorohexane (C_6F_{14}) as the recommended candidate replacement agent for the DoD. Perfluorohexane, meets all performance requirements, but has a long atmospheric lifetime, which means it could contribute to global warming. Therefore, the US Environmental Protection Agency tentatively approved perfluorohexane for military fire fighting use only. Air Force Headquarters (AF/CE/LGM) subsequently decided not to recommend fielding of this chemical in view of this and possible future more stringent restrictions. As a result, WL/FIVCF has initiated a preliminary research effort to develop a second generation fire suppressant which will meet the original Halon 1211 replacement agent requirement as well as having a low to zero global warming potential (GWP). This proposal provides for continuation of this preliminary effort.

7. **Project Description:**

The prior research work identified several classes of chemical compounds not in commercial production that exhibit fire suppressant characteristics equal to or better than halons. The most promising of these include bromofluoroalkenes, fluoroiodocarbons, aromatic bromine-containing halocarbons, polar-substituent bromocarbons, and non-volatile precursors. The objective of this effort is to develop a "drop-in" clean, environmentally safe streaming fire suppressant to replace Halon 1211 used in flightline and aircraft portable fire extinguishers. The candidate compounds will be examined for their global environmental impact to insure that those that are filtered through to advanced testing have low/zero ODP and GWP. The major uncertainties at present are their toxicity and manufacturability. The primary focus in the initial screening of these compounds will be to perform preliminary toxicity evaluations. A manufacturing/synthesis assessment will be conducted in the initial evaluation to insure that the emerging candidates are

able to be manufactured at reasonable cost. The best candidates to emerge from screening will be manufactured in a small pilot plant to create sufficient quantities for medium and large scale testing, materials compatibility testing, and validation testing. Coordination with manufacturers for technology transfer in the latter stages of the program will be an important consideration for matching Air Force demand to private sector capacity. The Air Force is taking the lead in exploring this class of chemicals. Close coordination and collaboration with the Army, Navy, industry and academia is being exercised to avoid possible duplication and to take advantage of synergistic opportunities.

Tie to Tri-service Environmental Quality R&D Strategic Plan:

Pillar Thrust Area:	3.H
Requirements Category:	3.II.4.c
Work effort:	Tech Demo

8. Expected Payoff:

The successful completion of this research effort will provide the Air Force and other DoD components with a replacement for Halon 1211, a heavy ozone depleter. A Halon 1211-like agent is required for use in Air Force and other DoD component flightline and portable aircraft fire extinguishers due to that agent's excellent fire suppression capability and zero residue and non-corrosive characteristics. These characteristics are essential for fighting aircraft engine and manned compartment fires. Due to the widespread use of Halon 1211 fire extinguishers in the civilian community, the agent developed in this research effort will also be of significant benefit to that sector.

9. Milestones/Accomplishments:

1. Complete survey compounds/fire suppression mechanisms	03/94
2. Complete manufacturing/synthesis assessment	05/94
3. Complete global environmental impact assessment	09/94
4. Complete preliminary toxicity evaluations	12/94
5. Complete initial laboratory testing	03/95
6. Complete stability evaluations	09/95
7. Complete evaluation of phosphonitrilic compounds	07/96
8. Complete evaluation of organometallic	09/96
9. Complete evaluation of silanes/siloxanes	12/96
10. Select two top non-halocarbon candidates	02/97
11. Complete advanced toxicity testing	07/97
12. Complete medium scale fire suppression testing	09/97
13. Select top non-halocarbon candidate	11/97
14. Complete large scale testing	06/98
15. Complete operational validation	10/98
16. Final report	12/98

Small scale testing of CF3I using a modified UL test procedure has been carried out against a 100 ft^2 JP8 pool fire. The series of tests indicated that CF3I is a powerful fire suppressant that, in some cases, outperforms Halon 1211. Concerns about the cardiotoxicity resulted in several blends of CF3I and less problematical HFCs being evaluated at laboratory scale. Screening of all blended agent combinations with CF3I as the basis was completed using a combination of cup burner and bench scale streaming agent testing. Materials tested included HFC-227ea, HFC-236fa, PFC-614, and HFE-A. Several tests to combine the laboratory results were conducted in an outdoor small scale test environment with several of the most promising blends. The strategy is to maintain the effectiveness of CF3I while at the same time reducing its cardiotoxic potential via blending with HFCs. Cup burner of the blended agents has been completed with results showing a linear relationship of fire suppression when the agents are combined in azeptropic or near azeotropic conditions.

Synthesized the first of a new class of fire suppressants that are unlike the previously proposed substitutes for Halon 1211, all of which have been halocarbons. The new compound, a phosphonitrilic (PN), has a laboratory cup burner of approximately 0.3%, ten times better than Halon 1211. Currently larger quantities of the PN are being synthesized to carry out initial toxicity testing and additional small scale testing. Prospects are high for developing a suitable and more effective replacement for Halon 1211 within the next two years. In addition, the chemical has zero ozone depletion and global warming potential. Toxicity factors are under investigation.

10. Transition Plan:

The effort will produce a streaming agent purchase specification and technical documentation covering materials compatibility, combustion products, and fire extinguisher performance tests results. These products will be transitioned to the Air Force Material Command, Aeronautical Systems Center (ASC/YOC) for the Engineering Manufacturing Development (EMD) phase. The EMD effort will, if necessary, develop and test any modifications to flightline and aircraft portable fire extinguishers to accept the new agent and will implement an agent change-out program. The same data will be provided to the Army, Navy, and industry for application, as appropriate. Industry has the capability to produce the chemical compounds of interest in laboratory quantities. It is believed that a cost effective volume production capability can be established for the selected compound(s). This should be confirmed by the manufacturabilty assessment to be conducted as part of the currently on-going effort.

11. Funding: $(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	850	383	400	950	0	2,583
AirForce	600	200	100	194	400	1,494

12. Performers:

This project is being managed by the Air Base Fire Protection and Crash Rescue Systems Section (WL/FIVCF), Wright Laboratory, at Tyndall AFB, Florida. A SETA Subtask has been awarded to accomplish the first phase of the research effort, i.e., through initial laboratory testing. A task order contract and/or additional SETA Subtasks, as appropriate, will be used for the follow-on phases. The SETA contractor, Applied Research Associates, has subcontracted the initial research work to the New Mexico Engineering Research Institute. Preliminary toxicity efforts are being conducted by the Armstrong Laboratory (AL/OET). An expert panel will be established to conduct initial and periodic reviews of the technical approach; data collection procedures; interpretation of results; and environmental, regulatory, and safety issues that may have a impact on agent viability. Throughout the program , actions by standards making organizations involved in fire protection, including the National Fire Protection Association (NFPA), and by environmental regulatory agencies - in particular, the US Environmental Protection Agency - will be reviewed to ensure that agents developed are in full compliance with planned standards and regulations. Other players in the fire research arena that will be used or consulted include, but are not limited to, the University of Florida, chemicals manufacturers, and fire extinguishing equipment manufacturers. Close coordination, to include joint testing, will be maintained with the Army and Navy to ensure the selected agent meets their mission requirements.

13. Principal Investigator:

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14. Keywords:

Halon 1211, Fire Suppression, Halocarbons, Bromocarbons, Fluoroiodocarbons, Bromofluoroalkenes, Phosphonitrilics, Silanes, Silox

SERDP FY96 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non-Ozone Depleting Refrigerants for Navy Chillers

3. **Agency:** U.S. Environmental Protection Agency (EPA)

4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)

5. **Project ID:** #309

6. **Problem Statement:**

The Navy currently has approximately 900 shipboard chillers using CFC-114 refrigerant for purposes of vital equipment cooling and comfort air-conditioning. Since by law, production of CFC-114 ceased on December 31, 1995, the Navy is seeking a suitable alternative refrigerant to retrofit its CFC-114 chillers as the supply of CFC-114 dwindles or convert the entire fleet to entirely different cooling plants. Retrofitting existing chillers instead of replacing these units would save the Navy in excess of $500 million. Projected unavailability of CFC-114 requires that the Navy commence retrofitting the fleet in the 1997 to 1998 time frame.

The EPA (Environmental Protection Agency) has been researching potential CFC-114 alternatives since 1988. Through this program, two non-ozone depleting, low global warming candidate alternatives (i.e., HFC-236ea and HFC-236fa) have emerged as especially promising. The Navy, through its own evaluation of several possible alternatives, has also concluded that HFC-236ea and HFC-236fa are among the most viable retrofit candidates. To meet the stringent retrofit deadlines, further evaluations of HFC-236ea and HFC-236fa must be completed prior to 1998. Toxicity testing of the chemicals, recognized as that element of the development program which requires the greatest time to complete and therefore, defines the critical path to success, has begun and is expected to be completed in 1996. Additionally, further laboratory performance and materials evaluations of the chemicals are required to identify which of the two candidates is superior.

7. **Project Description:**

In anticipation of meeting the Navy's retrofit needs, the EPA requested and received FY91, FY92, FY93, and FY94 SERDP funds for acquisition and laboratory evaluation of HFC-236ea. Work is progressing satisfactorily in concert with the Navy's performance testing of both HFC-236ea and HFC-236fa in a 125-ton chiller of the type used on ships. Evaluations of both chemicals along a parallel path will continue until such time as one chemical can be clearly identified as superior to the other. When a preference for one of the chemicals is decided, further work will concentrate on the preferred alternative.

Completion of toxicity testing sufficient to enable the Navy to safely commence retrofit of shipboard chillers with the selected alternative refrigerant will be the main thrust of the future work. Initial acute inhalation toxicity tests such as determination of the LC_{50}, cardiac sensitivity threshold, and developmental toxicity have been conducted for HFC-236ea with FY92 SERDP funds. FY93 SERDP funds were utilized for determination of the genetic toxicity and 90-day subchronic inhalation toxicity of HFC-236ea. Since toxicity data favored HFC-236fa over HFC-236ea, FY94 and future SERDP funds concern further engineering and toxicity studies of HFC-236fa.

The proposed program would complete all needed toxicity tests for HFC-236fa and complete all required toxicological evaluations for this preferred chemical, including evaluations imposed by the Navy as regards use of the chemical in confined spaces such as submarines. Completion of the program is anticipated in 1996.

Requested FY95-FY96 SERDP funds will also be used to procure quantities of HFC-236fa needed for the toxicity testing and for laboratory performance investigations which have been planned by both EPA and the Navy. The Navy has recently established a laboratory facility and installed seven shipboard-type air conditioning plants for performance investigations of CFC-114 alternatives. These air-conditioning plants are the same designs which are currently installed on the Navy's most sophisticated aircraft carriers, surface combatants, and submarines. The Navy also has developed plans to procure 6 additional shipboard-type air-conditioning plants for a second phase of laboratory performance investigations. It has been estimated that up to 15,000 pounds of HFC-236fa will be required for the toxicity and performance investigations. EPA will rely on Iowa State University to perform engineering studies of HFC-236fa and compatible lubricants to complement studies completed for HFC-236ea with FY91 and FY92 SERDP funds.

Engineering materials and lubricants compatible with the alternative refrigerants will be identified via NRML/APPCD in-house laboratory tests for use in the Navy's refrigerant performance investigations. Expansion of the thermophysical property database and determination of the heat transfer coefficients for HFC-236fa will also be accomplished with the requested FY94 funds and FY95 funding.

This work directly supports the goals of Pillar 3 (Pollution Prevention) in the Tri-Tri-Service Research Plan which has a goal to eliminate the use of ODS (ozone-depleting substances) as soon as possible. Specifically, the project supports work under Thrust 3F to identify safe, affordable chemical substitutes for ODS refrigerants.

8. Expected Payoff:

Building upon the success of previous work, it appears very likely that HFC-236fa will be selected to replace CFC-114 in Navy shipboard chillers. This would enable the Navy to quickly eliminate the use of CFC-114 without incurring the major expense of converting all existing chillers to new equipment. Once implemented by the Navy, it is anticipated that additional uses of HFC-236fa would be identified in the private sector to further eliminate the Nation's dependence on ODS's.

9. Milestones/Accomplishments:

1. Determine developmental toxicity and cardiac sensitivity	12/94
2. Complete additional HFC-236fa subchronic genetic toxicity tests	06/95
3. Procure additional quantities of HFC-236fa	11/96
4. Complete balance of toxicity tests for preferred chemical	09/96

Modelling and small-scale tests confirmed that both HFC-236ea and HFC-236fa were suitable near drop-in replacements for CFC-114 in the Navy's shipboard chillers. These tests confirmed that engineering performance, materials and equipment compatibility, and commercially available lubricants supported the selection of either of these new non-ozone depleting chemicals as a retrofit alternative to CFC-114.

10. Transition Plan:

Toxicity testing must be completed prior to commercialization of any chemical. Results of such tests will be reported to the Navy and chemical producers to allow timely decisions to be made regarding selection of preferred retrofit chemical, any equipment design or construction modification, and commercialization. Every attempt will be made to meet the retrofit deadlines set by the Navy.

11. Funding: $(K)

	FY91	FY92	FY93	FY94	FY95	FY96	TOTAL
SERDP	500	500	300	507	125	410	2342
EPA	50	50	150*	50*	0	0	300
TOTAL	550*	550	450	557	125	410	2642

* Most of these funds were for performance related activities not toxicity.

12. Performers:

Primary: EPA/NRML/APPCD with contracts to toxicity testing laboratories and chemical suppliers.

Other: Naval Medical Research Institute, Robert Carpenter
Naval Sea Systems Command, Joel Krinsky
Iowa State University (via EPA/Exxon Chemical Cooperative Research and Development Agreement), Michael Pate and Howard Shapiro

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14. Keywords:

Refrigerant, Chillers, Ships, Stratospheric Ozone, CFC-114, Toxicity